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DIELECTRIC ABSORPTION AND DIELECTRIC LOSS.

BY

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INTRODUCTION.

THE nature of the energy loss it dielectrics subjected to alternating stress is not completely understood. That dielectric absorption, as observed under continuous stress, must account for at least a part of the loss under alternating stress has long been recognized. Starting from Maxwell's analysis of the phenomenon of absorption, Rowland,[1] in 1897, derived the expressions for the resulting dielectric loss under alternating stress. In connection with various assumptions as to the ultimate nature of dielectric absorption, other similar expressions [2, 3] for the loss under alternating stress have been derived.

A somewhat different and more satisfactory method of showing the relationship between dielectric absorption and dielectric loss is that of von Schweidler,[4] who starts with the experimentally determined curve of charge or discharge current as related to time. Then by use of the principle of superposition (Hopkinson-Curie) he is enabled to write the general expression for the alternating current resulting from an harmonic e.m.f., applied at any instant in the past. This current is in two components, which give the value of the loss and also the increase over the value of the geometric capacity of the condenser under test. Should the dielectric have a permanent residual conductivity the loss due to this conduc-

tivity must be added to the loss due to the dielectric absorption. So far satisfactory tests of the accuracy of this analysis are wanting.

Rowland developed a sentitive electrodynamometer, many new forms of bridge connections, and with his co-workers [5] made numerous studies of the behavior of dielectrics under alternating stress. He notes, however, that he could find in his experiments only qualitative agreement with the expression derived from Maxwell. K. W. Wagner,[6] applying Maxwell's theory to certain simple cases, has reported broadly qualitative agreement only, in the changes occasioned by variations of frequency and of temperature. The failures of efforts of this character to check observation with theory are largely due to the fact that no dielectric has ever been found which meets Maxwell's fundamental assumptions, and the further fact that the phenomenon of absorption itself, under continuous voltage, is not clearly defined and is not in accord with the explanation offered by Maxwell.

The method of von Schweidler is not subject to these difficulties, in that it starts immediately from an experimental curve. Until recently, however, no check was possible by reason of the difficulty of determining this experimental curve for very short intervals of time following the instant of the application of voltage for charge, or of short circuit for discharge. It is necessary to note the type of variation, during a time interval relatively short compared with the alternating period at which the loss is to be studied. The only tests so far reported, which seem to approach these conditions, are those of F. Tank.[7] Using a pendulum for short interval contacts, and a succession of periods of alternate charge and short circuit, he obtained a discontinuous point by point curve of charge for very short intervals, on several condensers. The losses were measured by an electrodynamometer method. A reasonable agreement with von Schweidler's expressions was obtained on three out of six condensers.

PURPOSE OF THIS WORK.

The present work reports a series of absorption and loss studies on a condenser of high grade impregnated paper insulation. The charge and discharge curves have been recorded

by means of a vacuum tube amplifier and oscillograph to within .001 sec. of the instant of application of voltage, and at values of 500, 1000, and 1500 volts, corresponding to those at which the alternating loss measurements were made. The loss was measured on a Schering bridge of high accuracy and screened in accordance with the method described elsewhere by the author.[8] The alternating frequency was 60 cycles. The loss as computed from von Schweidler's expressions is compared with the measured values.

COMPUTATION OF LOSS DUE TO ABSORPTION.

Let the reversible charge or discharge current due to absorption be:

$$i = E \cdot \varphi(t) \tag{1}$$

in which E is the applied continuous e.m.f., and $\varphi(t)$ a continuously decreasing function of the time t, as measured from the instant of application of voltage or the beginning of short circuit. $\varphi(t)$ does not contain the initial transient, but does contain a constant term determined by the constants of the condenser under test.

By the principle of super-position:

$$\Delta i = \Delta E \cdot \varphi(t - \theta), \tag{2}$$

where ΔE is applied at time $\theta < t$.

If E is of the form, $E = E_0 \sin p \cdot \theta$; $p = 2\pi f$.

$$i_t = \int_{-\infty}^{t} \frac{dE(\theta)}{d\theta} \cdot \varphi(t - \theta) \cdot d\theta \tag{3}$$

$$= pE_0 \int_{-\infty}^{t} \cos p\theta \cdot \varphi(t - \theta) d\theta. \tag{4}$$

Noting that i_t will be periodic and substituting $t - \theta = u$, we have:

$$i_t = pE_0(A \cos pt + \beta \sin pt), \tag{5}$$

$$\left.\begin{aligned} A &= \int_0^{\infty} \varphi(u) \cdot \cos pu \cdot du, \\ B &= \int_0^{\infty} \varphi(u) \cdot \sin pu \cdot du \end{aligned}\right\} \tag{6}$$

If $\varphi(t)$ is of the form

$$\varphi(t) = \beta \cdot C \cdot t^{-n}, \tag{7}$$

and $1 > n > 0$, von Schweidler gives the following values for A and B.

$$\left.\begin{aligned} A &= \left(\frac{1}{p}\right)^{1-n} \cdot \beta \cdot C \cdot \Gamma(1-n) \cdot \cos\frac{(1-n)\pi}{2}, \\ B &= \left(\frac{1}{p}\right)^{1-n} \cdot \beta \cdot C \cdot \frac{\pi}{2\Gamma(n)\cos\frac{(1-n)\pi}{2}}, \end{aligned}\right\} \tag{8}$$

in which C is the geometric capacity and $\Gamma(n)$ the Eulerian "gamma" function.

If $\varphi(t)$ is of the form

$$\varphi(t) = m \cdot C \cdot e^{-\alpha t}, \tag{9}$$

then for all values of α

$$\left.\begin{aligned} A &= C\,\frac{m\alpha}{p^2+\alpha^2}, \\ B &= C\,\frac{mp}{p^2+\alpha^2}. \end{aligned}\right\} \tag{10}$$

In either case the dielectric loss, due to absorption, under alternating voltage will be:

$$W = 2\pi f \cdot C\,\frac{E_0^2}{2} \cdot B \tag{11}$$

and the apparent capacity:

$$C^1 = C\left(1 + \frac{A}{C}\right). \tag{12}$$

Tank found that equation (7) best fitted his results, n being less than 1, and he used the values of equation (8). His values of loss as computed and observed are of the same order of magnitude, but show considerable variation in absolute values and in uniformity.

In our results, as given below, there is a much better agreement between the measured values and those computed by

use of equations (9) to (12) inclusive. The negative exponential relation of (9) is obviously the more rational basis, in that the absorption current tends to a finite value at zero time. It is the relation proposed by Maxwell and found in many experiments. The relation of formula (7) as used by Tank, however, indicates infinite current at zero time. Notwithstanding this fact many experimental curves, especially those of complex materials (see below), appear to conform to formula (7) rather than formula (9).

EXPERIMENTAL RESULTS.

The test condenser consisted of a central brass tube 91 cm. long and 2.54 cm. in diameter, on which were spiralled 25 layers of .004″ thick manila paper in the usual manner of the insulation of high voltage cables. On the outside a lead foil electrode 70 cm. long, and flanked by two similar guard electrodes, each 5 cm. long, was closely applied. The drying evacuation, and impregnation of this condenser and other electrical properties have been given elsewhere by the author.[8] Its final steady resistance at 22° C. is about 8×10^{13} ohms.

MEASUREMENT OF ABSORPTION.

Figs. 1 and 2 give typical charge and discharge curves. These were taken with a 3-stage vacuum tube amplifier, and

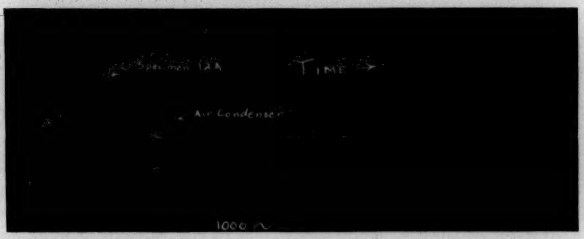
FIG. 1.

Charging current curve. Specimen 12A at 500 volts and 22.5° C. January 4, 1929. S.R. = 1000 Ω. I.R. = 110,000 Ω.

electromagnetic oscillograph as described by S. K. Waldorf,[9] with modifications for this work. The special switch, spring operated, with double contacts, as indicated in the diagram of

connections, Fig. 3 provided means for an initial low sensitivity to relieve the oscillograph of the shock of the geometric charge. This is indicated by the first low peak on the record.

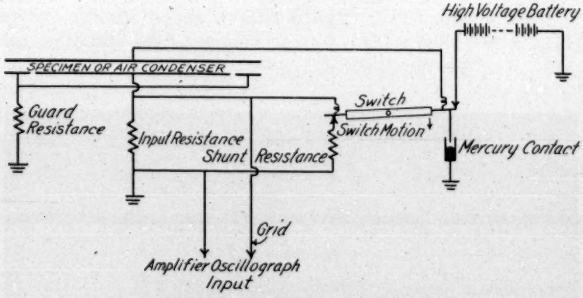
FIG. 2.



Discharge current curves at 1500 volts and 20.7° C. December 24, 1929. S.R. = 1000 Ω. I.R. = 60,000 Ω.

The duration of this interval is seen to be of the order of .0005 sec. Full sensitivity is then applied and the absorption curve may be read to within .0015 sec. or better. The circuit tran-

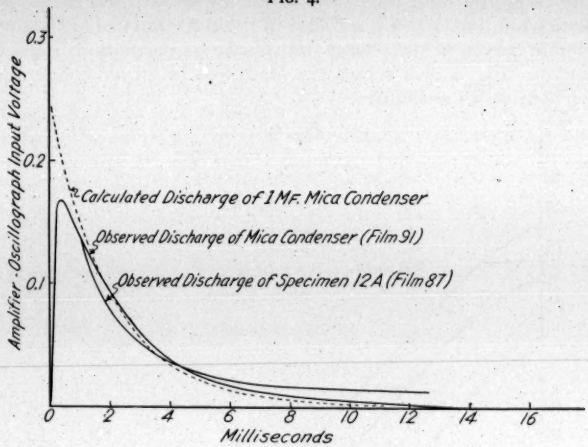
FIG. 3.



Principal connections for obtaining discharge current curves.

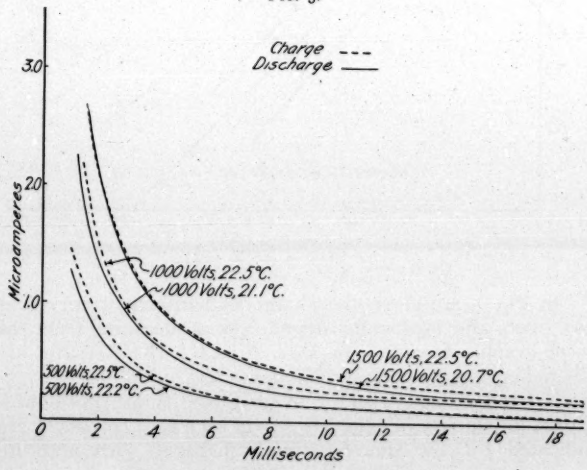
sient is negligible at these values. The accuracy of the response of the oscillograph was tested by an air condenser and series resistance so chosen as to give a discharge curve of approximately the same shape and magnitude as that studied;

FIG. 4.



Comparison of discharge of mica condenser through 2000 Ω with discharge of specimen 12A at 500 volts.

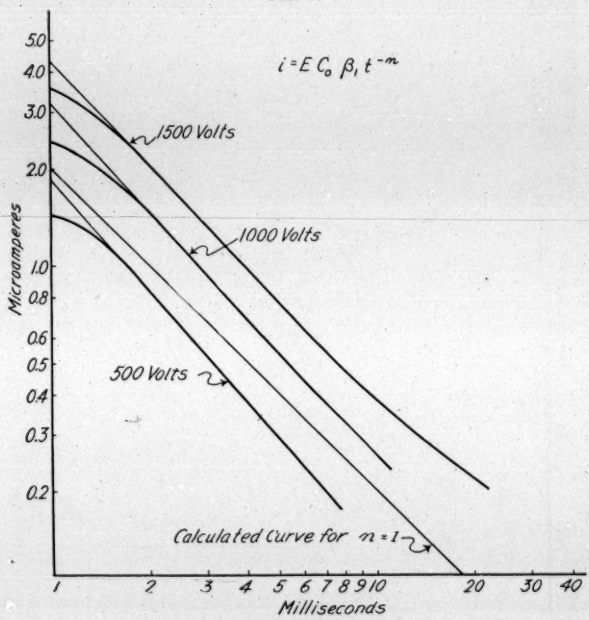
FIG. 5.



Charge and discharge current curves of specimen 12A.

the computed and observed values are shown in Fig. 4. A somewhat better check is found in the continuity of the logarithmic curves of the charge and discharge currents in Figs. 6 and 7. Fig. 2 also shows the discharge of an air condenser without series resistance.

FIG. 6.



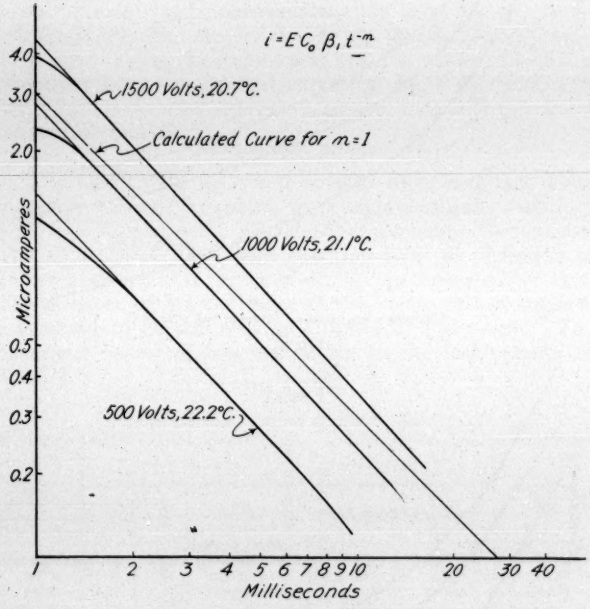
Charge current curves. Specimen 12A at 22.5° C.

In Fig. 5 are given the charge and discharge curves at 500, 1000, and 1500 volts respectively as measured from the oscillographic records. In Figs. 6 and 7 these results are plotted in logarithmic coördinates as a test for the law of equations 7 and in Figs. 8 and 9, in semi-logarithmic coördinates as test for the law of equation 9. In each case the slopes are indicated for the shortest time consistent with accurate

reading of the film, and apparent uniformity of the law of variation.

Considered over the whole range of the records, the agreement throughout with equation (7) is quite close. In this case the measured slope for each of the three voltages is closely the same, and gives a value of n of 1.11 for charge and

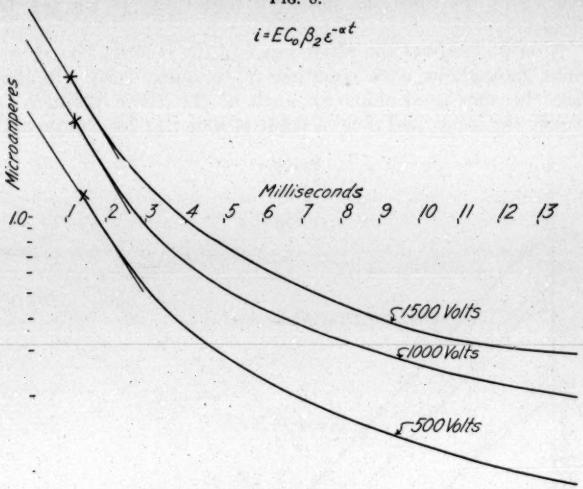
FIG. 7.



Discharge current curves. Specimen 12A.

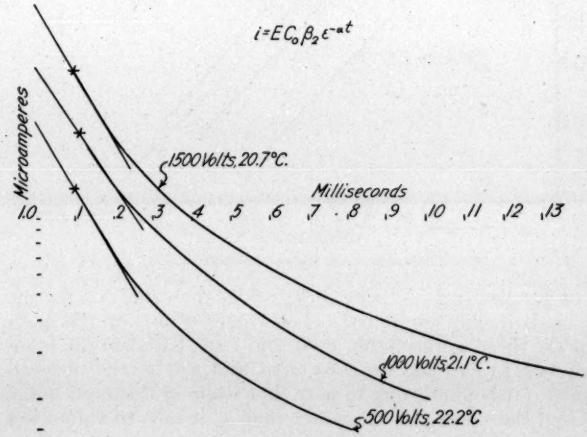
1.06 for discharge. Using these values the value of β for any point is readily computed. The values of β/E on discharge for the three voltages 500, 1000, and 1500, based on the interval .002 to .003 sec. are 2.65, 2.52, and 2.57 $\times 10^{-3}$ respectively. It is interesting to note that while in this brief initial period the value of n is greater than 1, it falls to values less

FIG. 8.



Charging current curves. Specimen 12A at 22.5° C.

FIG. 9.



Discharging current curves.

than 1 if the charge or discharge is continued over a long period; thus beyond one minute n for charge was found to be .685 and for discharge .886.

The curves of Figs. 8 and 9 show little evidence of general agreement with the negative exponential relation of formula (9). The only region approximating a straight line is that towards zero time. This however is the region in which we are interested. The slopes are approximately constant below .002 sec. and approximately the same for the three voltages; the mean values of α being 575 for charge and 581 for discharge. Using the mean value 578, the values of m/E are computed from the original curves, giving 6.05, 5.66, 5.75 (av. 5.82) for the discharge curves at 500, 1000, and 1500 volts respectively.

MEASUREMENT OF LOSS.

The losses were measured at 500, 1000, and 1500 volts (effective values), 60 cycles, on a high sensitivity Schering bridge, equipped with electrostatic screening throughout. The accuracy of the bridge was tested by the insertion of known resistances in series with the specimens under test. The method, within the range of the values of loss studied, was found to be accurate to within $\frac{1}{2}$ of 1 per cent. The measured values of loss are shown in the last column of Table I.

TABLE I.

Comparison of Computed and Measured Values of Loss.

Volts	$\varphi(t) = B \cdot C \cdot t^{-n}$			$\varphi(t) = m \cdot C \cdot e^{-\alpha t}$			Loss Watts Obs.
	n	$\frac{B}{E}$	Loss Watts Comp.	α	$\frac{m}{E}$	Loss Watts Comp.	
500	1.06	2.65	.00042	578	6.03	.00032	.00033
1000	1.06	2.52	.0017	578	5.66	.00131	.00132
1500	1.06	2.57	.00377	578	5.75	.00295	.00297
Average	1.06	2.58		578	5.82		

Table I also contains the values of loss as computed from the absorption, assuming the latter to obey the simple laws of equations (7) and (9). In making the computations the average values of the constants of the discharge curves have been used. It will be observed that there is an unusually

close agreement between the measured values and those computed on the assumption that the absorption follows equation (9).

The agreement is less satisfactory when using the law of equation (7) though the computed values are still surprisingly close to those as measured. Although absorption curves seem to follow this law quite closely at times, and in fact in the cases here reported, it is obvious that it can not be the correct relation for very short time intervals by reason of the approach of the current to infinite value.

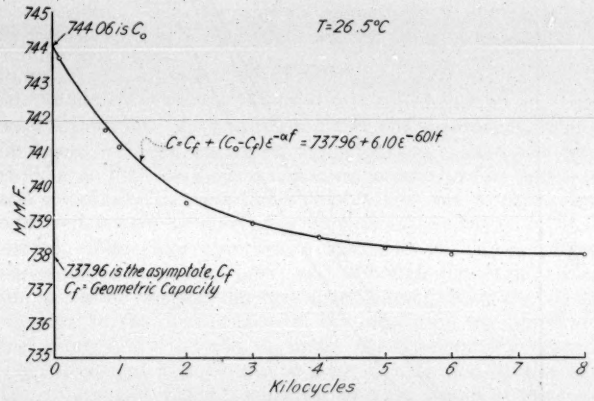
The measured loss contains also a constant value due to the final constant resistance, and any loss which may arise in an irreversible absorption current. The former is negligible in the present case. Fig. 5 indicates the presence of a small irreversible component of the charging current in two of the curves and none in the third. It is probable that in this type of insulation there is always some irreversible absorption present. As in our case the amount is small, and as there is some doubt as to its influence in causing loss, this factor has been neglected. The discharge curves have been used in the computations as giving more nearly the true reversible absorption curves. The resistance curves Fig. 11 also indicate some departure from Curie's law of proportionality between absorption and voltage.

INCREASE IN CAPACITY.

It is well known that a condenser possessing absorption has under alternating stress a capacity which decreases with increasing frequency, reaching a constant "geometric" capacity at infinite frequency. The increase over the geometric value for any frequency is given in formula (12). The value of A, as given by von Schweidler (formula (7)), governs the variation with the frequency, if n is less than 1, as observed by Tank. We have found n greater than 1, and in this case formula (7) does not hold, nor can the integral of formula (6) be evaluated. This is a further difficulty in any attempt to use formula (7) for expressing the absorption curve. These objections do not obtain in using formula (9). The A term in formula (12) for the apparent capacity is now found in formula (10) and can immediately be evaluated in terms of α and m. Using the values of Table I, we find $A = .007$.

Fig. 10 shows the apparent capacity C^1 as related to the frequency between 100 and 8,000 cycles, as measured on an accurate high frequency bridge, supplied with a pure sine wave Noting that $C^1 = C(1 + A) = 1.007\ C$, we have the possibility of computing the geometric capacity from the value at any lower frequency and checking it with the value indicated by the empirical equation of the curve between the capacity and frequency. The measured value of capacity at 60 cycles is 743.8 mmf. The value of the geometric capacity as taken

FIG. 10.



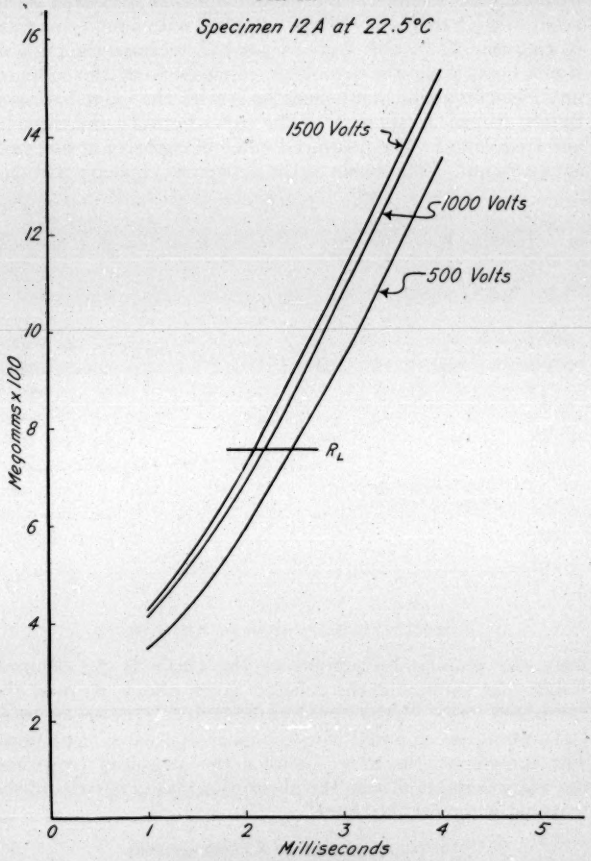
Capacity vs. frequency. Specimen 12A, April 19, 1929.

from the empirical equation of the curve is 737.96 mmf. Using this value and the relation given above, we find the computed value of the apparent capacity C^1 at 60 cycles is 743.1 mmf. as compared with the measured value 743.8 mmf. The agreement, therefore, between the measured value and the value computed from the absorption characteristics of the material is remarkably close.

INITIAL RESISTANCE AS A CAUSE OF LOSS.

It has been proposed by Sinjelnikoff and Walther [10] that the resistance of a dielectric is a constant quantity, absorption being a polarization effect, and that this resistance determines

FIG. 11.



Variation of apparent resistance with time.

in the i^2r relation the amount of dielectric loss. Tank [7] makes a similar proposal for liquids. The absorption curves of Figs. 1 and 2 give no indication of an initial constant value of current. In Fig. 11 are drawn the apparent resistance curves, as taken from the absorption curves. These show no indication of an initial constant value. Further if the measured losses are used for computing a single value of resistance which would account for the loss, we reach almost exactly the same value, viz: 7.58×10^8 ohms at each voltage. This value has been marked on the curves as R_L, and it is evident that much lower values of resistance are indicated by the initial absorption current. Our observations thus appear in contradiction to the assumption of an initial constant value of resistance.

CONCLUSIONS.

When this work was begun, it was hoped that an approximate agreement, say to the same order of magnitude, might be found between measured and observed values. It was recognized that the dielectric material studied, while excellent as an insulator, is nevertheless highly complex in character, and well known as possessing anomalous properties in high degree. The close agreements indicated in Table I have therefore come as a surprise, and although the work is still in the initial stages, the condenser having been chosen at random for the development of the measuring equipment, it has seemed worthwhile to make this preliminary report. The agreement is not quite so close as indicated by the last two columns of Table I, since the average values of the constants, as taken from the drawn curves, have been used. It is believed that the results are accurate to within 5%, the error arising chiefly in the transcription of the film records, in the determination of the constants, in an as yet uncontrolled small variation of temperature, and in the possible influence of a small irreversible component of charging current.

The following are the principal conclusions from the work:

(*a*) Dielectric absorption charge and discharge current curves have been observed to within .001 sec. of their initial values.

(*b*) The dielectric absorption properties of a good grade of impregnated paper have been studied between .001 and .025 sec. at 500, 1000, and 1500 volts.

(*c*) In this region the decay of the current curves is fairly well represented by $i = E.C.\beta t^{-n}$, with n greater than 1. The relation $i = E.C.me^{-\alpha t}$ is indicated only for a short initial portion of the curves.

(*d*) Dielectric loss on the same condenser has been measured at 60 cycles, and at voltage 500, 1000 and 1500.

(*e*) A close agreement is found between measured loss and that computed on the assumption that dielectric absorption accounts for all the loss.

(*f*) Agreement is also found between measured and computed values of the increase in capacity with decreasing frequency, as due to dielectric absorption.

(*g*) No indication is found of an initial constant dielectric conductivity as sometimes proposed.

ACKNOWLEDGMENTS.

Thanks are due to the skill and resourcefulness of Dr. S. K. Waldorf in the measurement of absorption, and of Mr. A. Banos, Jr., in the bridge adjustments and measurement of power, and to Dr. W. B. Kouwenhoven for many helpful suggestions. The work has been done in the laboratory of Electrical Engineering, of the Johns Hopkins University. Grateful appreciation is also expressed to the Utilities Research Commission of Illinois, whose financial support has made possible the active prosecution of the work.

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A NOTE ON THE HIGH GRID RESISTOR AMPLIFIER.

BY

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Communication No. 41.

MULDER and Razek[1] have shown that the effective mutual conductance of a three element "vacuum" tube can be greatly increased by operating the tube in a grid circuit containing a high resistance. Their treatment of the problem does not show clearly the conditions which must be met in order to obtain this high mutual conductance without a discontinuous and non-reversible part in the characteristic.

With the plate voltage and the filament current constant in a three element tube, the plate current and the grid current are related to the grid voltage as shown by Figs. 1 and 2. The first of these is of course perfectly familiar and needs no explanation. The second is a composite of three currents. For very small values of grid voltage the current is mainly electron current from the filament. This of course falls off rapidly as the grid is made more and more negative with respect to the filament. There is the leakage current over the base of the tube and the other external parts. This current is usually negligible if the surfaces are clean and the tube is kept in a dry atmosphere. This leakage current *increases* as the grid voltage is made more negative. The third and important component depends on the presence of gas in the tube. It is this component which plays the all important part in the type of amplifier under discussion. The positive ion current to the grid *decreases* as the grid is made more and more negative because the number of positive ions decreases as the electron current from the filament to the plate is decreased. As the subsequent discussion will show, it is the point of inflection (A) in the grid current characteristic that is of primary interest. This characteristic in the immediate

[1] Razek and Mulder, *J. O. S. A., and R. S. I., 18*, p. 466, 1929.

FIG. 1.

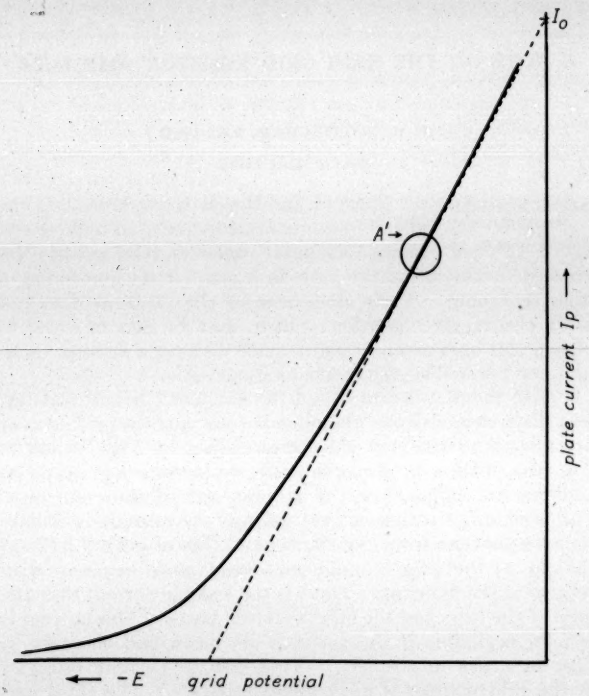


Plate current characteristic of vacuum tube.

neighborhood of the point of inflection can be represented very accurately by the equation

$$i_g = -i_0 - mE, \qquad (1)$$

where i_0 = constant,

m = a constant (the slope at (A)),

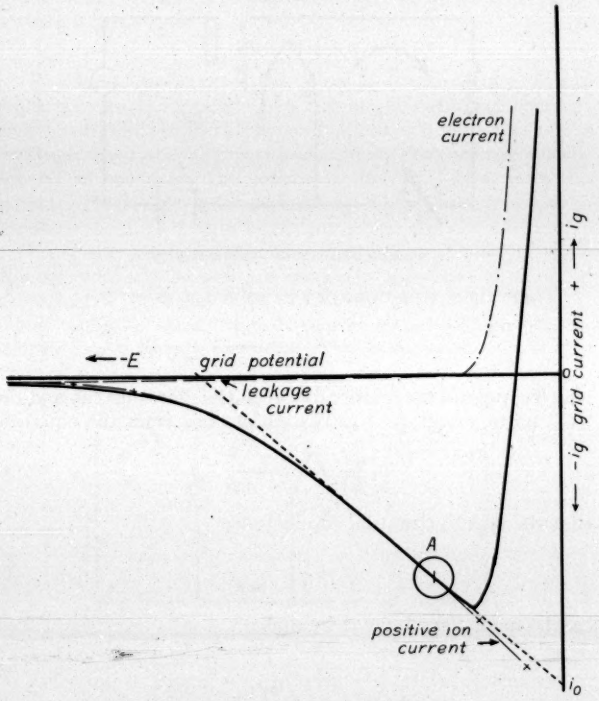
i_g = the grid current,

and E = the grid voltage.

The corresponding part of the plate current characteristic can also be represented by a straight line

$$I = I_0 + gE, \qquad (2)$$

FIG. 2.



Grid current characteristic of vacuum tube.

where I_0 = constant,

g = constant (mutual conductance or slope at A' of Fig. 1),

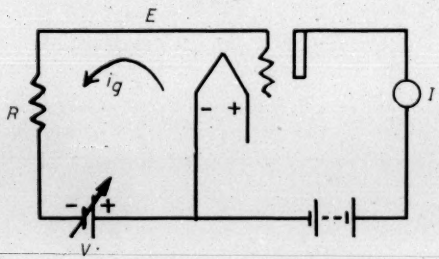
I = plate current,

E = grid voltage.

Referring to the circuit sketched in Fig. 3, we have a third relationship given by

$$V = Ri_g + E. \tag{3}$$

FIG. 3.



Schematic diagram of three element tube circuit.

These three equations can be solved to give

$$I = I_0 - \frac{gRi_0}{1 - mR} + \frac{g}{1 - mR} V, \tag{4}$$

which expresses the relation between the plate current and the "C" battery voltage V. We see at once from the equation

$$\frac{\Delta I}{\Delta V} = \frac{g}{1 - mR} \tag{5}$$

that the effective mutual conductance

$$g' = \frac{g}{1 - mR} \tag{6}$$

can be made very large if we make

$$R = \frac{1}{m} \tag{7}$$

in the limit.

It is at once obvious that in order to make use of this high effective mutual conductance severe requirements must be met as regards filament, plate and grid batteries and also the tube must be so constructed that the amount and kind of gas does not change with time. It is thought that this require-

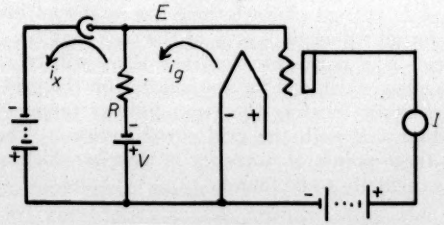
ment can be met if the tube is so designed that the metal and glass parts can be thoroughly baked out under good vacuum conditions and purified argon or some other inert gas is introduced to produce the required gas pressure. The "balanced bridge" circuit could probably be used to make battery maintenance a little easier.

APPLICATIONS.

The most important application to which a tube of this character can be applied is to the amplification of thermocouple potentials since this type of amplifier is in a sense really "voltage sensitive," that is, its sensitivity does not necessarily depend on producing the voltage as an "IR" drop as in the usual photoelectric cell application which has become so popular.

From the preceding discussion, it is not at once obvious that there would be any advantage in this type of tube for photoelectric or other high resistance problems. The following analysis shows that here too an advantage can be realized under certain conditions.

FIG. 4.



Schematic diagram of photoelectric cell and three element tube circuit.

Referring to Fig. 4, we can write the following equations:

$$V = E + R(i_g - i_x) \text{ (From Fig. 4)}, \tag{8}$$

$$I = I_0 + gE \text{ (From Fig. 1)}, \tag{9}$$

$$i_g = -i_0 - mE \text{ (From Fig. 2)}. \tag{10}$$

These equations are essentially the same as (1), (2) and (3) above. In this case, V is to be constant and the relation

between i_x (the photoelectric current) and I (the plate current) is of interest. Solving these equations, we have

$$I = I_0 + \frac{g(V + Ri_0)}{1 - mR} + \frac{g}{1 - mR} Ri. \tag{11}$$

This can be more simply written

$$I = K + g'Ri, \tag{12}$$

where K = constant

and

$$g' = \frac{g}{1 - mR}. \tag{13}$$

Again the sensitivity is represented by

$$\frac{\Delta I}{\Delta i_x} = \frac{gR}{1 - mR} \tag{14}$$

and this is very large when

$$R = \frac{1}{m}.$$

From the equations, we see that for values of R less than $1/m$ the plate current characteristic has no discontinuity and is stable for all values of V or i_x as the case may be. On the other hand, if R is greater than $1/m$ there will be a discontinuous region which can be marked out on the grid current characteristic by locating the two points of tangency of the line of slope $1/R$ with the grid current curve. The region between these points of tangency is that in which a discontinuity is certainly to be found.

A very complete treatment of the subject of "Direct-current Amplifiers" by Ebbe Rasmussen, Ann. d. Phys. (5) *2*, 357 (1929), has come to my attention since the writing of this paper. Although Rasmussen's discussion of the question of gas in a three element tube is made from a different point of view, his results and those presented here are in agreement.

ON THE ASYMMETRIC VIBRATION OF A CONCRETE BAR.

BY

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§1. INTRODUCTION.

ACCORDING to the Report [1] of the Building Research Board of the Department of Scientific and Industrial Research published in 1924, Young's moduli for a concrete bar obtained by the application of the tension and compression tests, show a very remarkable difference, namely, $E_t/E_c = 1.27$, where E_t and E_c represent the values of Young's moduli due to the tension and compression, respectively.

If we assume the above experimental fact to be true, independent of the amount of strain, a very interesting phenomenon may be supposed to occur in the case of a longitudinal vibration of a concrete bar constructed of similar material to that used in the above experiment—viz. that every element of the bar, on being excited to vibrate longitudinally, must be subject to a kind of asymmetric vibration owing to the difference in Young's moduli at the opposite sides of its equilibrium position.

On this consideration, the writers using this simple conception of the longitudinal vibration, have here treated of the asymmetric vibration caused by a cantilever made of a concrete bar of the same constituents as those in the experiment mentioned above, the physical constants and dimensions being tabulated as follows.

TABLE.

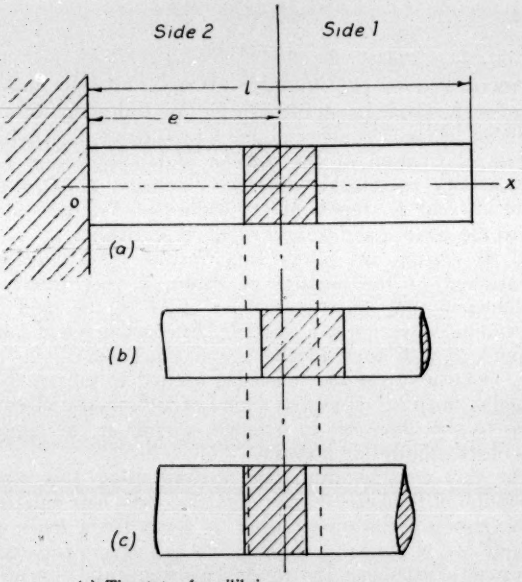
ρ (density)	E_t	E_c	l (length)	ω (sectional area)
2.58	3.26×10^{11}	[C.G.S.] 4.13×10^{11}	22 c.m.	1 cm.^2

[1] "Concrete and Constructional Engineering," Vol. 19 (1924), p. 709.

In the above report, the density of the bar used at the time of the experiment was not given, so that we have been obliged to use the value of the density at the time when it was constructed,[2] which is that given in the above table.

In applied physics it must be an interesting matter to determine any property of the material by means of the sound which it emits when struck. Indeed, it is from this idea that, at the end of this paper, we have added an article on Fourier's analysis of the asymmetric vibration.

FIG. 1.



(*a*) The state of equilibrium,
(*b*) The state when the element displaced to side 1,
(*c*) The state when the element displaced to side 2,
Side 1, the tension side for the element,
Side 2, the compression side for the element.

[2] Assuming that the densities of cement and sand are 3.1 and 2.65, respectively.

§2. AMPLITUDE AND FREQUENCY OF VIBRATION.

In Fig. 1, let us take a fixed plane at $x = e$ perpendicular to the length of the bar, and take an element having a circular section, the central plane of which is at the position $x = e$, in the state of equilibrium.

We have assumed first that the displacement [3] is taken as

$$u_\theta = u_r = 0,$$
$$u_x = \text{function of } x \text{ and time } t,$$

secondly, that there is no dissipation of energy along the whole length of the bar during the motion, and also that the plane of the clamped end is such that the elastic wave is perfectly reflected on it.

The equation of a longitudinal vibration is as follows,[4] for the sake of simplicity denoting u_x by ξ

$$\frac{\partial^2 \xi}{\partial t^2} = \frac{E}{\rho} \frac{\partial^2 \xi}{\partial x^2}, \tag{1}$$

where E = Young's modulus.
ρ = density of the bar.

The initial and boundary conditions necessary for the case are as follows:

$$\begin{aligned} &1.\ \xi \text{ and } \frac{\partial \xi}{\partial t} = 0 \quad \text{at} \quad x = 0, \\ &2.\ \overline{xx} = 0 \quad \text{at} \quad x = l, \\ &3.\ \xi = 0 \quad \text{at} \quad t = 0. \end{aligned} \tag{2}$$

The solution of (1) satisfying (2) is

$$\xi = \sum s A_s \sin n_s t \sin \left(\frac{n_s^2 \rho}{E} \right)^{1/2} x, \tag{3}$$

where

$$\cos \left(\frac{n_s^2 \rho}{E} \right)^{1/2} l = 0.$$

[3] Hereafter, usual notations of the displacement and stress in cylindrical coördinate are used.

[4] Strictly speaking, this is not quite exact because there is certain amount of lateral inertia expressed by $\sigma K^2 \frac{\partial^4 \xi}{\partial t^2 \partial x^2}$, where σ is Poisson's constant and K the radius of gyration of the cross section about the central line. But in the present case, the error caused by neglecting this effect is assumed to be insignificant.

In order to avoid any complication of the problem, we have assumed that the displacement is expressed simply by the principal mode of vibration, i.e., $s = 1$, the effect of the higher harmonics of the vibration being so small that they are negligible compared with that of the principal mode of vibration.

Then equation (3) becomes

$$\xi = A \sin nt \sin\left(\frac{n^2\rho}{E}\right)^{1/2} x, \tag{3'}$$

and the displacement of the element at $x = e$ is

$$\xi = A \sin nt \sin\left(\frac{n\rho}{E}\right)^{1/2} e. \tag{3''}$$

The expression of the energy which the element has at the opposite two sides of the fixed plane at $x = e$, namely the tension and compression sides, denoted briefly by 1 and 2 respectively, are

for side 1:

$$\frac{1}{2}\rho\omega\left(\frac{\partial\xi_1}{\partial t}\right)^2 + \frac{1}{2}E_1\omega\left(\frac{\partial\xi_1}{\partial x}\right)^2 = \phi_1,$$

for side 2:

$$\frac{1}{2}\rho\omega\left(\frac{\partial\xi_2}{\partial t}\right)^2 + \frac{1}{2}E_2\omega\left(\frac{\partial\xi_2}{\partial x}\right)^2 = \phi_2,$$

in which the sectional area ω has been taken as unity in the subsequent calculations.

It is plain that the energy ϕ_1 and ϕ_2 must be always equal, under the assumption that there is no dissipation of energy as mentioned above.

So that we have

$$\phi_1 = \phi_2. \tag{4}$$

From (3) we have

$$\left.\begin{aligned}\frac{\partial\xi_1}{\partial t} &= A_1 n_1 \cos n_1 t \sin\left(\frac{n_1^2\partial}{E_1}\right)^{1/2} x \\ \frac{\partial\xi_2}{\partial t} &= A_2 n_2 \cos n_2 t \sin\left(\frac{n_2^2\rho}{E_2}\right)^{1/2} x\end{aligned}\right\}. \tag{5}$$

Now n_1 and n_2 are 2π times the frequencies of the vibra-

tions at the sides 1 and 2, and therefore by the well known properties of a stationary wave, or which is the same thing, by condition 2 of (2), we have

$$n_1 = \frac{\pi}{2l}\sqrt{\frac{E_1}{\rho}}, \quad \text{and} \quad n_2 = \frac{\pi}{2l}\sqrt{\frac{E_2}{\rho}}.$$

From equation (4) and (5), taking e as $\frac{1}{2}l$, and choosing a time t at the instant when the element passes the fixed plane at $x = \frac{1}{2}l$, it being the moment when the potential energy of the element at the sides 1 and 2 are both equal to zero and the kinetic energies of the same are a maximum, we have

$$\frac{A_1}{A_2} = \sqrt{\frac{E_2}{E_1}}. \tag{6}$$

Returning to equation (3″), if we assume one of the values of A given in (6), the expression of the displacements of the element at the opposite two sides of the fixed plane $x = \frac{1}{2}l$, will be obtained by the following equations

$$\left.\begin{aligned} \xi_1 &= \frac{1}{\sqrt{2}} A_1 \sin\left(\frac{\pi}{2l}\sqrt{\frac{E_1}{\rho}}\right)t \\ \xi_2 &= \frac{1}{\sqrt{2}} A_2 \sin\left(\frac{\pi}{2l}\sqrt{\frac{E_2}{\rho}}\right)t \end{aligned}\right\}. \tag{7}$$

The period T of the asymmetric vibration of the element is now easily reduced by the following simple calculation, i.e.,

$$\begin{aligned} T = &\text{ (half the period of the vibration at side I)} \\ &+ \text{ (half the period of the vibration at side 2)} \\ = &\ 2l\sqrt{\rho}\left\{\frac{1}{\sqrt{E_1}} + \frac{1}{\sqrt{E_2}}\right\}, \end{aligned} \tag{8}$$

then 2π times the frequency N is

$$N = \frac{\pi}{l\sqrt{\rho}} \Big/ \left(\frac{1}{\sqrt{E_1}} + \frac{1}{\sqrt{E_2}}\right). \tag{9}$$

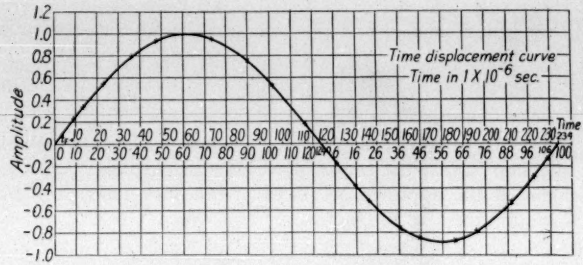
§3. FOURIER'S ANALYSIS OF THE ABOVE RESULT.

Let us construct a time-displacement curve from equation (7), introducing the relation of (6), and assuming one of the values of A.

In the present case, we have taken $\frac{1}{\sqrt{2}} A_1 = \text{unity}$.

In Fig. 2, a curve is drawn, in which the positive and

FIG. 2.



negative senses represent the amplitudes corresponding to the tension and compression side, respectively.

Then the problem left to us is to analyse this curve by the method of Fourier's analysis, taking 2π times its frequency as expressed in equation (9).

For the sake of simplicity, however, we have done it by means of the so-called practical Fourier's analysis,[5] originated by Clairaut and Lagrange.

Now, the problem is to obtain $a_0, a_1, a_2, \cdots, b_1, b_2, b_3, \cdots$, in the expression

$$\xi = a_0 + a_1 \cos Nt + a_2 \cos 2Nt + a_3 \cos 3Nt + \cdots \\ b_1 \sin Nt + b_2 \sin 2Nt + b_3 \sin 3Nt + \cdots \qquad (10)$$

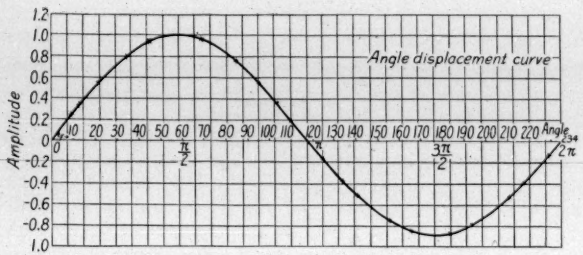
However, we have here restricted the problem conveni-

[5] Clairaut, "Hist. de L'Acad. Paris," p. 545.
Lagrange, "Misc. Taurin." (i), 1759, p. 1.
"Misc. Taurin." (iii), 1762–5, p. 259.
Whittaker and Robinson, "Calculus of Observation," p. 260–284.

ently, as the 12 values of ξ, i.e., ξ_0, ξ_1, ξ_2, ξ_3, $\cdots$ ξ_{11}, were given by the actual curve, corresponding to the values of the abscissa viz. 0, $\frac{\pi}{6}$, $\frac{2\pi}{6}$, $\frac{3\pi}{6}$, $\cdots$ $\frac{11\pi}{6}$ respectively.

For convenience in treating the analysis, we have changed the variable Nt to x, the angle-displacement curve shown in Fig. 3, being thus obtained from the time-displacement curve

FIG. 3.



shown in Fig. 2, and, after some calculation, we have obtained the following series of values

$$a_0 = \frac{0.1127(2+\sqrt{3})}{12}, \qquad a_1 = 0,$$

$$a_4 = \frac{-0.1127(\sqrt{3}-1)}{12}, \qquad a_5 = 0,$$

$$a_2 = \frac{-0.1127(1+\sqrt{3})}{12}, \qquad a_3 = 0,$$

$$b_1 = \frac{1.8873}{2}, \qquad b_2 = 0,$$

$$b_3 = b_4 = b_5 = 0.$$

The result to be obtained is now

$$\xi = \frac{0.1127}{12}\{(2+\sqrt{3}) - (1+\sqrt{3})\cos 2x - (\sqrt{3}-1)\cos 4x - (2-\sqrt{3})\cos 6x\} + \frac{1.8873}{2}\sin x. \quad (11)$$

The points plotted with this equation are shown in Fig. 3. The final result is now

$$\xi = \frac{0.1127}{12}\{(2+\sqrt{3}) - (1+\sqrt{3})\cos 2Nt - (\sqrt{3}-1)\cos 4Nt - (2-\sqrt{3})\cos 6Nt\} + \frac{1.8873}{2}\sin Nt. \quad (12)$$

where $N = 26850$.

The points plotted with this equation are shown in Fig.2. It is quite clear that the calculated values are very nearly in coincidence with those of the original values, the maximum error being only of about the order of 1/1000.

§4. SUMMARY.

1. The fact of $E_t \neq E_c$, obtained by the tension and compression tests of a concrete bar, has given us an interesting suggestion that in a concrete bar the longitudinal vibration shows a kind of asymmetric vibration, and consequently, the time-displacement curve of any element of it, by which the amplitude and frequency for the two types of vibration —namely those of the tension and compression sides—can be calculated, has been obtained.

2. By the practical method of Fourier's analysis, the harmonic expression of the above time-displacement curve has been obtained, and its close coincidence with the original time-displacement curve has been obtained.

In conclusion the writers wish to express their hearty thanks to Professor O. Miyagi for his kind guidance, and also to Asst. Prof. S. Uchida who gave us much valuable advice and information especially with reference to the properties of concrete.

THE HERSCHEL EFFECT AND THE FAILURE OF THE RECIPROCITY LAW.*

BY

A. P. H. TRIVELLI and V. C. HALL.

Introduction.—The diminution of developable density produced by a second exposure to light of long wave-lengths is known in photography as the "Herschel" effect. The amount of the Herschel effect is dependent, like other photographic effects, upon the intensity of the light used, both for the first exposure to blue-violet light and for the second exposure to infra-red light. These relations have been studied previously by other investigators. Thus, W. Leszynski [1] states that only by making the infra-red exposure at low intensity was he able to obtain the Herschel effect on photographic plates that had not been sensitized with potassium bromide. With higher intensities the density increased instead of decreasing. The developability of an original latent image can therefore be either increased or decreased by the secondary exposure to infra-red radiation, the effect depending upon the intensity of the light source and the spectral absorption of the filter. The relation of the intensity of the exposing lights to the Herschel effect and the so-called failure of the reciprocity law are therefore complicated. W. Leszynski used an infra-red filter which transmitted light to which the plate was so insensitive that exposure to a light source of 3.10^8 visual M.C.S. behind this filter gave no noticeable developability. Within an intensity range of 1 : 75, he could not detect any failure of the reciprocity law as regards the reduction of density produced. Lüppo-Cramer [2] repeating these experiments, however, found a failure of the reciprocity law when the intensity of the infra-red radiation was varied.

In his experiments, W. Leszynski found that if in the first exposure to blue light the intensity and time of exposure were varied, the energy being kept constant, a failure of

* Communication No. 387 from the Kodak Research Laboratories.

[1] *Z. wiss. Phot.*, 24: 275 (1926).

[2] *Z. wiss. Phot.*, 24: 380 (1927).

the reciprocity law was observed, since as the intensity of the blue light decreased the Herschel effect disappeared.

The work reported in this paper has been extended over a larger range of intensities in the pre-exposure than that used by previous investigators and two different photographic materials have been employed, which show interesting divergences in their behavior. Lüppo-Cramer [3] has studied the Herschel effect on plates desensitized with phenosafranin and in this investigation employed pre-exposures using different intensities of light. The German investigators, including H. Arens and J. Eggert,[4] interpret their investigations by the aid of the expression for the failure of the reciprocity law originally given by Schwarzschild.[5] As was shown by E. Kron,[6] Thalen,[7] and L. A. Jones with his collaborators, E. Huse and V. C. Hall,[8] the relation between density and intensity for the photographic plate is expressed by the Schwarzschild equation over a very limited range of intensities only, and over a greater range it is necessary to use a considerably more complicated expression.

Exposure.—The first exposures were made in a Jones reciprocity sensitometer,[9] which is a time-scale sensitometer of the sector wheel type. To eliminate intermittent exposures the exposures were made during only one revolution of the wheel.

The intensities used are given in Table I together with times of exposure and maximum meter-candle-seconds incident at each intensity. The exposures were all made to light of the standard color temperature of 2500° K. Sets 1 to 4, inclusive, were made with a 500-watt monoplane filament lamp, unscreened; sets 5 to 8, inclusive, were made with a 100-watt monoplane filament lamp behind three sheets of diffusing glass. Intensity changes in the first four sets were made by moving the lamp in a carefully diaphragmed tunnel;

[3] *Loc. cit.*

[4] *Zur Sensitometrie desensibilisierter Schichten, Z. wiss. Phot.*, **26**: 111 (1928).

[5] *Astrophys. J.*, **11**: 89 (1900).

[6] *Publ. Astrophys. Observ. in Potsdam*, No. 67 (1913).

[7] *Monthly Not. Roy. Astr. Soc.*, **75**: 159 (1915).

[8] *J. Opt. Soc. Amer.*, **7**: 305 (1923); **7**: 1079 (1923); **11**: 319 (1925); **12**: 321 (1926); **13**: 443 (1926); **14**: 223 (1927).

[9] L. A. Jones, *J. Opt. Soc. Amer.*, **7**: 305 (1925); **12**, 321 (1926).

in the last four both distance and effective area of the source were used to obtain the desired value of illumination. A careful photometric check was made between sets 4 and 5 to calibrate the low intensity source in terms of the high. The absolute values of the higher intensities were checked on a precision photometer bench.

TABLE I.

Set.	Intensity.	Time (max.).	$I.t$ (max.).
1	1280.	0.125″	160
2	160.	.25″	40
3	20.	2.0″	40
4	2.5	16″	40
5	0.3125	2′8″	40
6	0.039	17′4″	40
7	0.0049	2°16′32″	40
8	0.00069	9°6′8″	20

Photographic Material.—Two sets of investigations were made: One on a pure silver bromide emulsion; and one on a commercial high-speed silver bromo-iodide emulsion. The silver bromide was precipitated with potassium bromide which contained less than 0.002 per cent. potassium iodide. An analysis of this emulsion by A. Ballard showed 0.03 per cent. free potassium bromide in relation to the total amount of silver bromide. With 4 minutes' development in pyro-soda at 68° F. (exposures were made to acetylene light screened to daylight with No. 79 Wratten filter) the silver bromide emulsion has a speed of 63 H. and D., a gamma of 1.12, and a fog of 0.07.

The high-speed silver bromo-iodide emulsion contained more than one per cent. free potassium bromide in relation to the amount of silver halide present. According to the investigations of H. Arens,[10] we should regard this emulsion as one sensitized to the Herschel effect with free bromide. With 5.2 minutes' development in pyro-soda at 68° F. (exposures were made in the same sensitometer that was used for the pure silver bromide emulsion), the high-speed silver bromo-iodide emulsion has a speed of more than 1000 H. and D. with a gamma of 0.8 and a fog of 0.14. During this investigation corrections were made for fog.

[10] *Z. physik. Chem.*, 114: 337 (1925).

The reciprocity failure of these emulsions was first determined. Development was effected at 17° C. with brush [11] in pyro-soda:

After five minutes, development was stopped with diluted acetic acid (1 per cent.) and the plates were fixed in an acid fixing bath.

The Failure of the Reciprocity Law on the Pure Silver Bromide Emulsion.—In the normal study of the relation between time and intensity in photographic exposure, sensitometric exposures are made on strips at different intensities over the range in question. The sensitometric strips are given ten exposures, the time doubling on each succeeding step, and the intensity held constant. When these are developed, Hurter & Driffield characteristic curves are drawn for each intensity. Usually the *gamma*, or the slope of the straight-line portion of the characteristic curve, is not independent of the exposure intensity but varies somewhat as the intensity is changed. If we plot a curve connecting gamma with intensity normally it will tend toward higher gammas, as the intensity is increased. In the pure bromide emulsion investigated, however, the opposite is true, and gamma decreased as intensity increased, as shown in Fig. 1. This reverse of the usual phenomenon has been observed before on an orthochromatic emulsion exposed to green light (tungsten screened with Wratten "G" filter) and also on Eastman 40 plates sensitized with Kryptocyanin and exposed to extreme red light only.

A general theory for the change of shape of characteristic curve with intensity shift has been published [12] and will be briefly reviewed here. In this theory, use is made of the knowledge that homogeneity of grain size is the chief factor

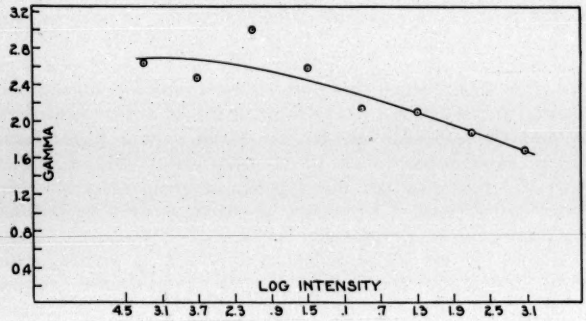
[11] *Cf.* W. Clark, *Phot. J.*, **65**: 76 (1925).

A	Sodium sulfite (water free)	280 grams	1 volume
	Sodium bisulfite	68 grams	
	Pyro	80 grams	
	Water	4 liters	
B	Sodium carbonate (water free)	300 grams	1 volume
	Potassium bromide	4 grams	
	Water	4 liters	
C	Water	4 liters	1 volume

[12] *J. Opt. Soc. Amer.*, **13**: 459 (1926).

controlling gamma. This fits in well with the effect of intensity on gamma in normal emulsions when it is assumed that the smaller and less sensitive grains become less effective more rapidly than the larger and more sensitive ones as

FIG. 1.



intensity is lower. The grain size-frequency curve of this emulsion is an exponential curve type.[13] By cutting down the effectiveness of the small grains the average will be transferred towards the larger grains and homogeneity will be lessened. In this theory we assume that sensitivity is some direct function of grain size.

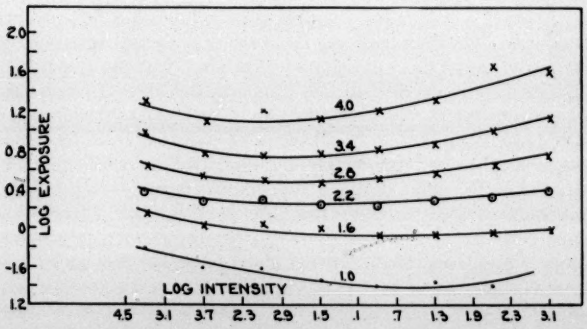
From this reasoning, the abnormal behavior of this present emulsion, in which gamma is decreased as the intensity is increased, must be explained by assuming that the sensitivity distribution is skewed in the opposite direction to the size-frequency distribution. This is more easily understood when it is remembered that in all cases of reciprocity failure it is the overall-sensitivity-frequency distribution, distinct from grain size-frequency distribution, which counts. In a normal emulsion it is probable that the methods of introducing sensitivity are such that the exposure sensitivity is roughly proportional to grain size, measured as projective area, and

[13] As pointed out by R. P. Loveland and one of us [J. FRANK. INST., 204: 193 (1927)] the shape of the frequency curve depends on the width of the classes of grain size. By taking narrower class sizes, the shape of the exponential curve changes into a skew distribution curve.

is not proportional to a higher power than the square of grain size. Considering that a grain becomes entirely developable if only one development nucleus is present and that a large grain has naturally more covering power than a small grain, *density* sensitivity should increase more nearly as the square of the grain size; or, perhaps, at a slightly higher power. If exposure sensitivity were to vary as the square of the grain size, then the overall—or density—sensitivity would vary approximately as the third power of the grain size. Since this pure silver bromide emulsion was ripened and sensitized to the limit, it would not be surprising to find the exposure sensitivity varying as a high power (or an exponential function) of grain size. This, together with the rather broad distribution of grain sizes present, could easily cause a frequency sensitivity curve to become less homogeneous as intensity is lowered.

Kron,[14] in his study of the density law of photographic plates, found that the best method of representation seemed to be to plot log $I \cdot t$ = log energy or log exposure, as a function of log intensity for a constant density. These "curves of constant density" are normally convex toward the log intensity axis, and have a minimum point, at which the energy necessary to produce a certain density is a minimum. A family of these curves, drawn for various constant densities,

FIG. 2.



[14] E. Kron, *Publ. Astrophys. Observ. in Potsdam*, No. 67 (1913).

is shown in Fig. 2. A comparison of these curves, individually, with those of other emulsions shows them to be quite normal. A study of the family of curves, however, shows that the position of the minimum point shifts toward low intensities as the density is increased. This is the reverse of what would be true if the gamma-intensity function were normal. We may conclude, then, that the individual grains of this emulsion are acting in the usual manner, but that because of some difference in grouping of the different sizes and sensitivities, some abnormality is shown in the action of the emulsion as a whole at different intensities.

From a consideration of these data, it was decided to concentrate the study of the Herschel effect on three intensities, one high, a second in the region of "optimal," or the most efficient intensity, and a third at a very low intensity. In this work, the first exposures were made in the reciprocity sensitometer with unfiltered tungsten radiation at a color temperature of 2500° K.

Set.	Intensities.	
I	160 mc.	(high intensity)
II	1.25 mc.	(optimum intensity)
III	0.00122 mc.	(low intensity)

Step exposures were given in the ratio of powers of 2.

The second infra-red exposure was made at right angles to the previous exposure in a non-intermittent sensitometer with 26 steps of $\sqrt{2}$ ratio, the maximum exposure being 5,791 seconds. The light source was a 500 c.p. monoplane filament lamp, kept at 104.8 volts (2700° K. color temperature) by a voltage regulator designed by A. L. Schoen, which maintained voltage constant to 0.7 volt. This reduces the intensity errors in the infra-red exposure to less than 3 per cent. The light was diffused by a piece of ground glass and the plate exposed at a distance of 1 meter from the diffusing diaphragm. This diaphragm had an aperture which allowed an illumination on the plate of 445 visual meter candles of white light. The infra-red Wratten filter No. 87, which transmits radiations only of wave-lengths longer than 700 $m\mu$, was placed between the diaphragm and the light source.

DISCUSSION OF DATA.

Every exposure was repeated five times and the densities were averaged. The data can be plotted in two ways: on a log $I \cdot t$ scale of the first, or white light, exposure; and on a log $I \cdot t$ scale of the second, or infra-red, exposure. Figs. 3 to 6 are obtained from the data for high intensity; Figs. 4 to

FIG. 3.

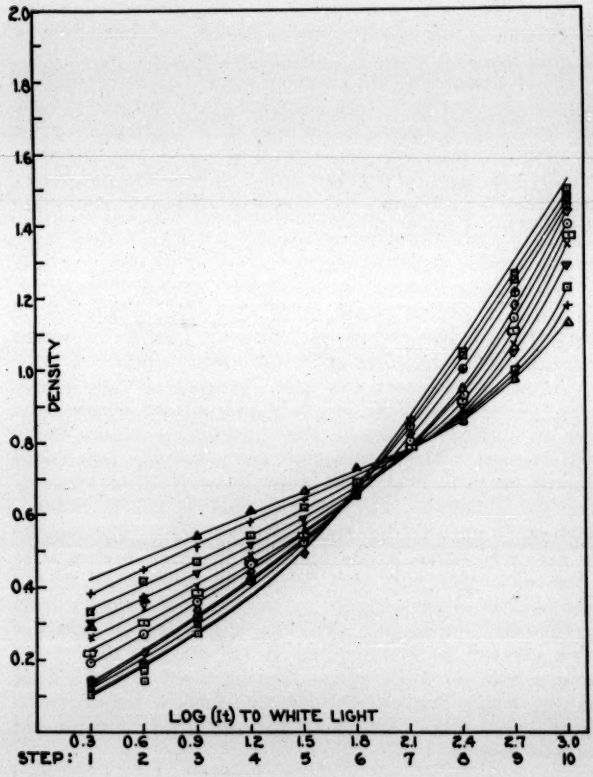
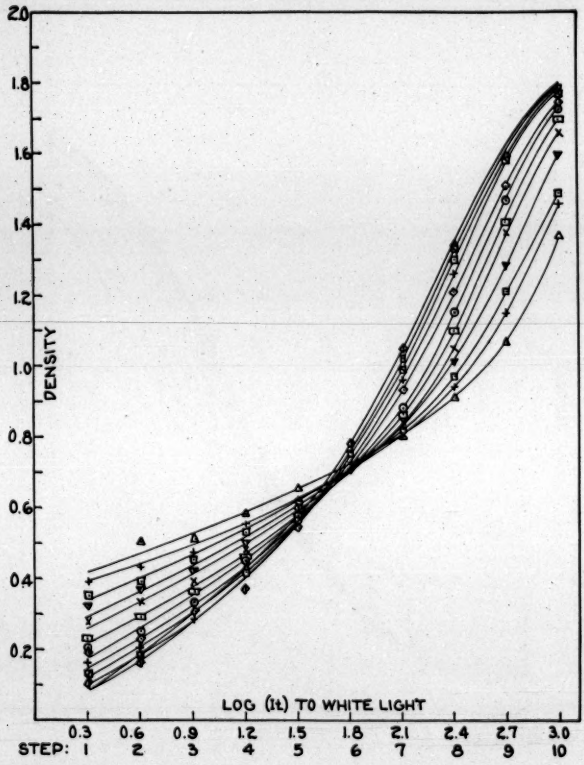


FIG. 4.



7 are obtained from the data with optimum intensity and Figs. 5 to 8 are obtained from the data for low intensity. Since the curves are not smoothed by any method, they show the neutral points * in Figs. 3, 4, and 5 as spots of

* That is the points where the infra-red exposure neither adds nor subtracts from the density produced when no second exposure is given.

many intersections on different places. As indicated in Table II, these spots shift with the different intensities used in the first exposure.

FIG. 5.

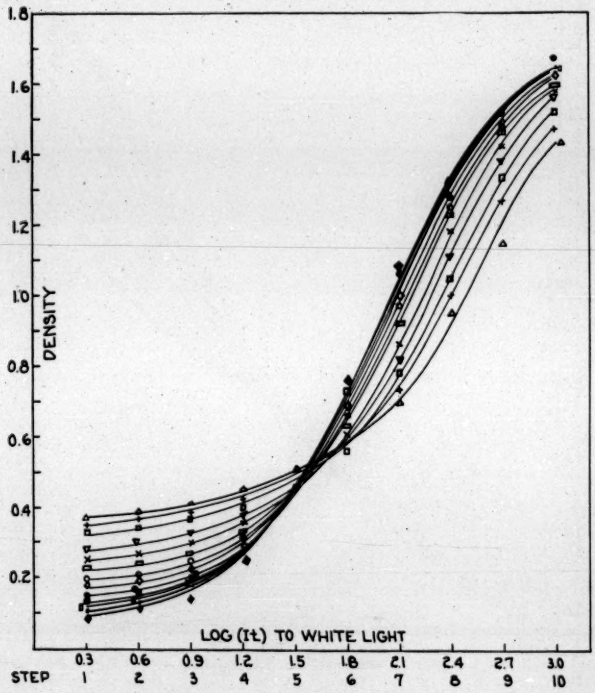


TABLE II

Neutral Spot

Int. White-light Exposure.	Log *Ew*.	Density.
160 mc.	±1.95	±0.75
125 mc.	±1.80	± .70
0.00122 mc.	±1.65	± .55

FIG. 6.

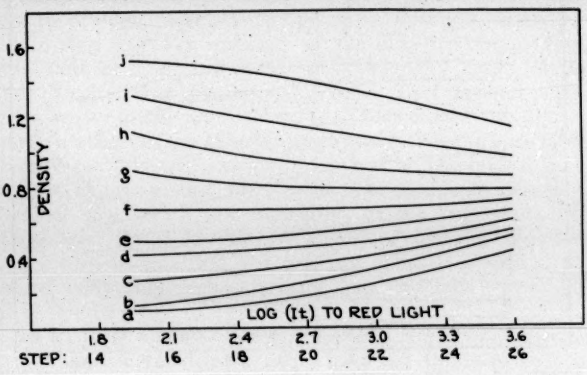

1.6
1.2
0.8
0.4
DENSITY
j
i
h
g
f
e
d
c
b
a
LOG (It) TO RED LIGHT
1.8 2.1 2.4 2.7 3.0 3.3 3.6
STEP: 14 16 18 20 22 24 26

FIG. 7.

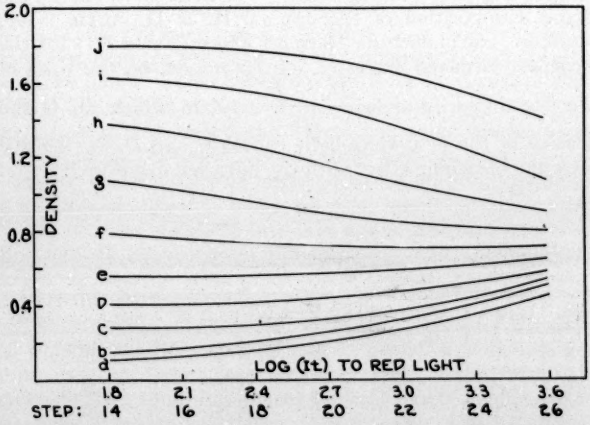
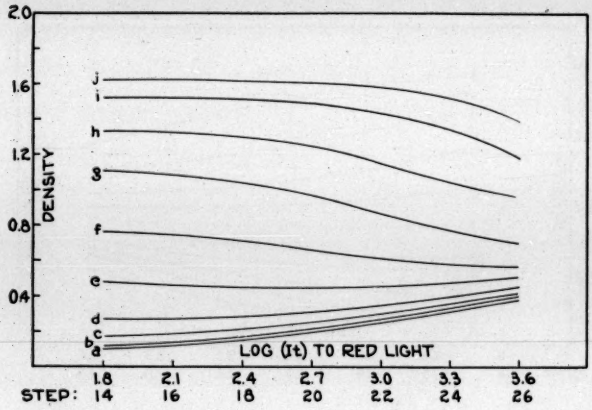

2.0
1.6
1.2
0.8
0.4
DENSITY
j
i
h
g
f
e
D
C
b
a
LOG (It) TO RED LIGHT
1.8 2.1 2.4 2.7 3.0 3.3 3.6
STEP: 14 16 18 20 22 24 26

FIG. 8.



In considering these data the magnitude of the Herschel effect is not readily determined. The final curve follows the shape and position of the original H. & D. curves. We, therefore, calculated the Herschel effect (Table III) for the strongest infra-red exposure, log $E_r = 3.60$, on the basis of the percentage formula: $\frac{D_w - D_r}{D_w} \cdot 10^2$ in which D_w is the density of the first white-light exposure, and D_r the density after the bleaching effect with the infra-red exposure.[15]

TABLE III.

The Herschel Effect for log $E_r = 3.60$

Values of $\frac{(D_w - D_r) \times 100}{D_w}$.

Step.	Log *Ew.*	When I = 160 mc.	When I = 1.25 mc.	When I = 0.00122 mc.
6	1.80	—	7.69	36.84
7	2.10	10.22	23.80	*35.18*
8	2.40	23.21	*32.08*	28.03
9	2.70	24.03	32.70	24.34
10	3.00	26.14	23.03	—

[15] *Cf.* A. P. H. Trivelli, *The Herschel Effect, J. Frank. Inst.*, **207**: 765 (1929).

This table shows the effect of the intensity of the first exposure on the Herschel effect. The maximum shifts from step 10 at high intensity to step 9 at optimum intensity and to step 6 at low intensity of the first exposure. This same shift of the maximum occurs in every step. With lower densities the maximum Herschel effect appears with low intensity in the first exposure. These data are in agreement with the statement of W. Leszynski [16] that the bleaching effect of the infra-red radiation depends on the intensity of the first exposure; but whereas he was unable to detect a Herschel effect with low intensities in the first exposure, it has been found in this investigation that on the pure silver bromide emulsion the greatest effect is obtained at low intensity, where the exposure time was four hours and thirty minutes.

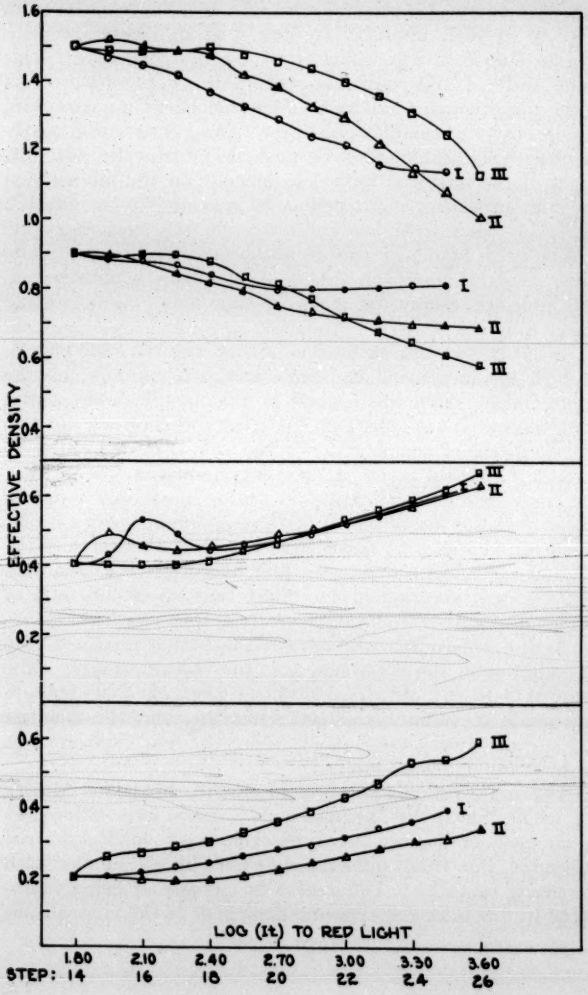
In all these cases we have compared the Herschel effects, in each instance using the same infra-red exposure on the latent image which was formed by the same incident white-light energy ($I \cdot t$ = constant). By interpolation we can also determine the bleaching action of the same infra-red radiation on first exposures made at different intensities where, after the same development, equal densities have been reached. These densities are obtained at three different energy levels. As shown in Fig. 9 we chose from the H. & D. curves of the original white-light exposures four densities: 0.2, 0.4, 0.9, and 1.5, and determined the effect that equal amounts of infra-red radiation would have on these four densities.

At the density 0.2, the infra-red radiation produces only an additional developability of the latent image. The greatest increase in density takes place where the first exposure was made to radiation of low intensity; and the smallest increase in density takes place where the first exposure was made at the optimum intensity.

The same ratio in increase of density holds for density 0.4, which is near the "neutral spot." Some large differences in increase of density are noticeable with small infra-red exposures, but these differences become much smaller with increasing exposure. Differences in increase of density produced by the infra-red exposure disappear as the neutral spot

[16] W. Leszynski, *loc. cit.*

FIG. 9.


EFFECTIVE DENSITY
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
I
II
III
LOG (It) TO RED LIGHT
1.80 2.10 2.40 2.70 3.00 3.30 3.60
STEP: 14 16 18 20 22 24 26

is approached, in spite of the fact that the total increase of density is still easily observable. In the first case where the primary density is 0.2, the greatest increase is from density 0.2 to 0.59. In the case where the primary density is 0.4 the greatest increase is from density 0.4 to 0.67. The lowest increase is in the first case from density 0.2 to 0.34; in the second case, from density 0.4 to 0.63.

The increase of densities produced by infra-red radiation at the first exposure with optimum intensity is in the first case from density 0.2–0.39; and in the second case, from density 0.4–0.61.

Summarizing, we see that with increasing density, produced by the first exposure, the increase of density caused by infra-red radiation is about the same if the first exposure is made at high intensity; and that with higher densities of the first exposure, approaching the neutral point, the increase of density with the low intensity decreases; and the increase of density with optimum intensity increases until it is of the same order as the increase of density at high intensity.

Within the experimental errors and within the range of intensities used in this investigation, we may say that at the neutral spot of the pure silver bromide emulsion there is no effect on the second infra-red exposure caused by the failure of the reciprocity law in the first white-light exposure.

At the density 0.9, the Herschel effect appears in various degrees depending upon the intensity of the first exposure and the time of exposure in the second infra-red radiation.

At the density 1.5, the phenomena are similar to those at 0.9, but the order is entirely changed. For instance, at the infra-red radiation $\log E_r = 3.15$ the Herschel effect increases in the order low, optimum, and high intensity with the first exposure; while at the density 0.9, this sequence is in reversed order.

The curves intersect at points corresponding to different amounts of infra-red radiation. To determine whether or not this variation is within the limits of experimental error more data must be collected.

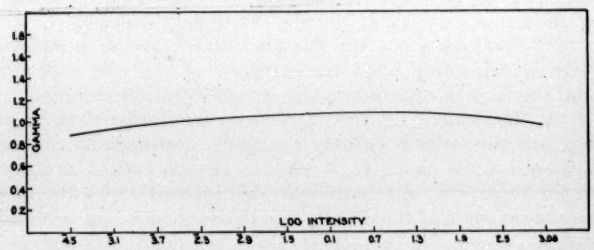
It is, however, evident that with time of exposure to the infra-red radiation a failure of the reciprocity law is observable.

In order to determine to what extent the above data could be generalized, it is necessary to extend the same investigations to another emulsion of a quite different kind. For this reason a super-speed silver bromo-iodide emulsion was chosen. This emulsion contained a relatively great amount of free potassium bromide (about one per cent.) which, under the proper conditions, gives a good Herschel effect.

The Failure of the Reciprocity Law of the Super-speed Silver Bromo-iodide Emulsion.—This emulsion is quite different from the previous one. It contains silver iodide in a homogeneous phase with silver bromide, i.e., a sensitizer for latent image formation, but a desensitizer for the Herschel effect. It contains, also, free potassium bromide, however, which is a desensitizer for the formation of the latent image, but a sensitizer for the Herschel effect. In this emulsion, therefore, we have sensitizers and desensitizers which react against each other. In the blue-light exposure the sensitizing for the latent image formation dominates; in the infra-red radiation the sensitizing for the Herschel effect dominates.

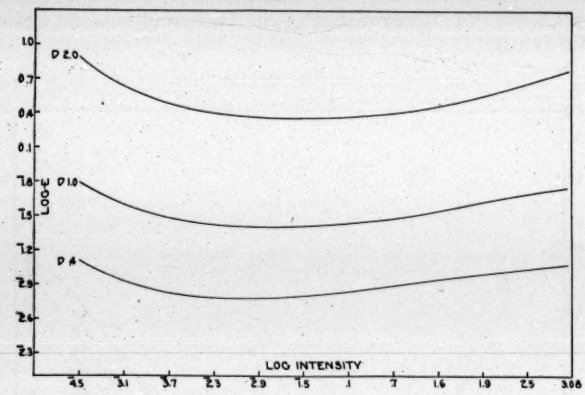
Fig. 10 shows the gamma-log intensity characteristic of

FIG. 10.



this emulsion. Gamma increases with increasing intensity, which is normal, but reaches a maximum at a fairly high intensity and shows at still higher intensities a slight decrease in gamma, similar to the silver bromide emulsion used in the first series of experiments. Fig. 11 shows the constant density curves, which are normal also.

FIG. 11.



Development and exposures were made under the same conditions used for the pure silver bromide with the one difference that the plates were developed for 4 minutes. The following intensities were chosen for the first exposure:

Set.		Intensities.
I	80 mc.	(high intensity)
II	0.625 mc.	(optimum intensity)
III	.00122 mc.	(low intensity)

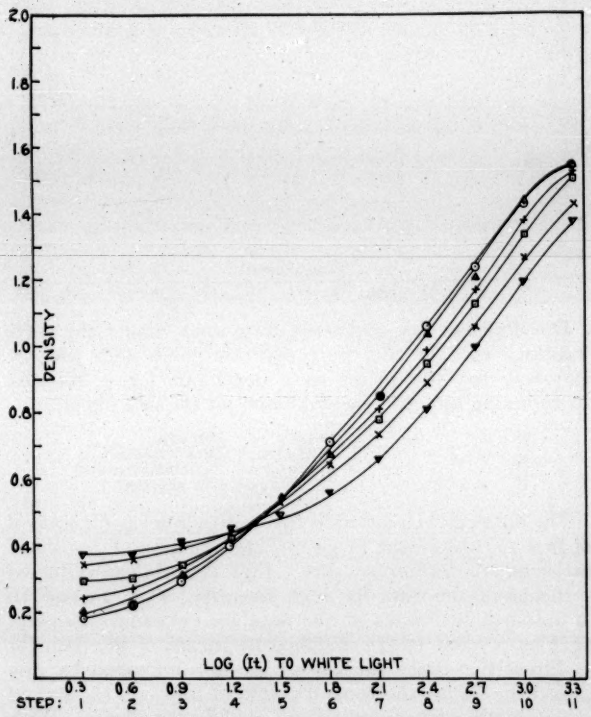
The data can be plotted in two ways: on a log $I \cdot t$ scale of the first or white-light exposure, and on a log $I \cdot t$ scale of the second or infra-red exposure. Figs. 12 and 15 are obtained by means of the data for high intensity; Figs. 13 and 16 are obtained by means of the data for optimum intensity; and Figs. 14 and 17 are obtained by means of the data for low intensity. Since the curves are not smoothed by any method they show the neutral points in Figs. 12, 13, and 14 as spots with many intersections at different places. With different intensities of the first exposure, these spots shift.

Neutral Spot.

Int. White-light Exposure.	Log *Ew*.	Density.
80 mc.	±1.35	±0.50
0.625 mc.	±1.05	± .35
.00122 mc.	±1.20	± .45

In comparing this shift with that of the pure silver bromide emulsion, it is noticeable that the two emulsions act quite differently.

FIG. 12.

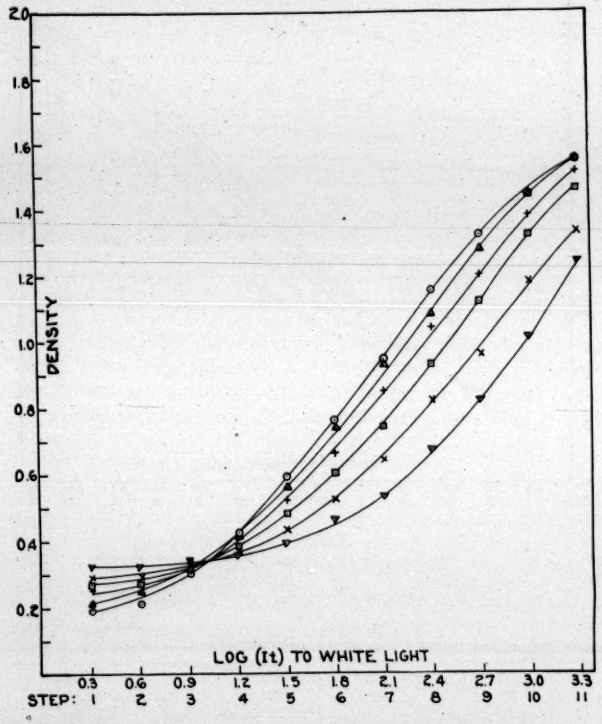


Figs. 15, 16, and 17 show the results plotted along log $I \cdot t$ for the infra-red exposure.

Calculating the Herschel effect for the strongest infra-red exposure log $E_r = 3.00$, we obtain the values given in Table IV. This table shows the effect of the intensity of the light used

in the first exposure on the Herschel effect. The total maximum runs from step 8 at high intensity to step 6 at optimum intensity, and to step 4 at low intensity. The

FIG. 13.



maximum for every step runs from step 11 to step 5 at optimum intensity to step 4, 3, and 2 at low intensity.

Again we find that with low intensity in the first exposure the greatest Herschel effects are obtainable at the lower exposures for white light. By interpolation we can find the amount of bleaching caused by the infra-red radiation on

FIG. 14.

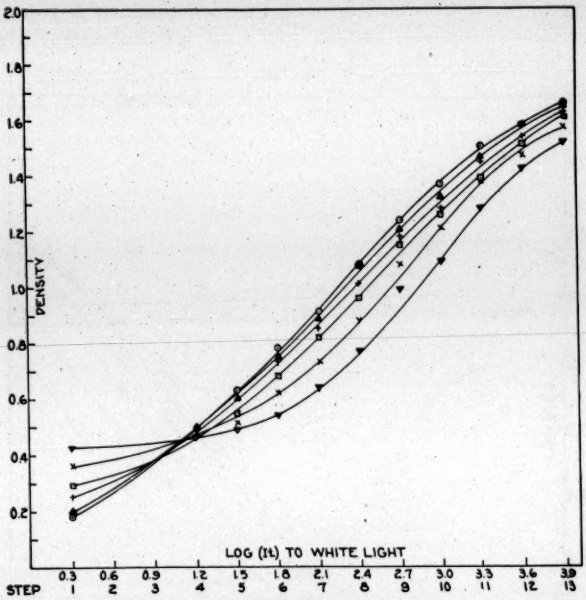


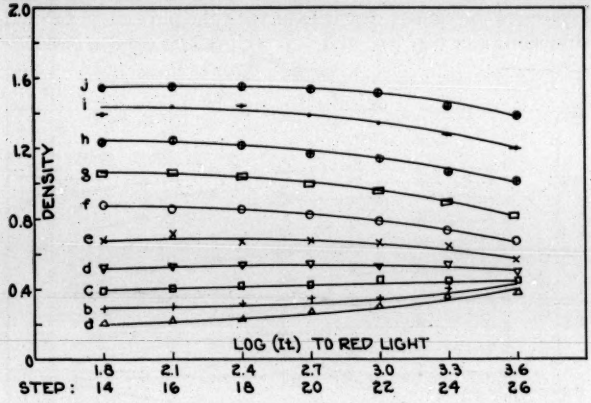
TABLE IV

The Herschel Effect for log $E_r = 3.60$

Values of $\frac{(D_w - D_r) \times 100}{D_w}$.

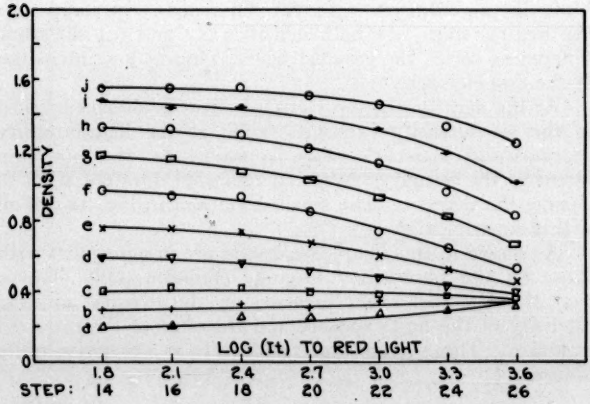
Step.	Log E_w.	When I = 80 mc.	When I = 0.625 mc.	When I = 0.00122 mc.
2	0.60	—	—	8.00
3	.90	—	—	22.22
4	1.20	—	10.00	31.64
5	1.50	5.77	*35.00*	31.18
6	1.80	19.23	47.36	28.03
7	2.10	19.51	*44.79*	20.80
8	2.40	21.36	*41.74*	20.43
9	2.70	18.03	*35.43*	14.66
10	3.00	15.49	*29.73*	7.79
11	3.30	8.60	*17.88*	7.36

FIG. 15.



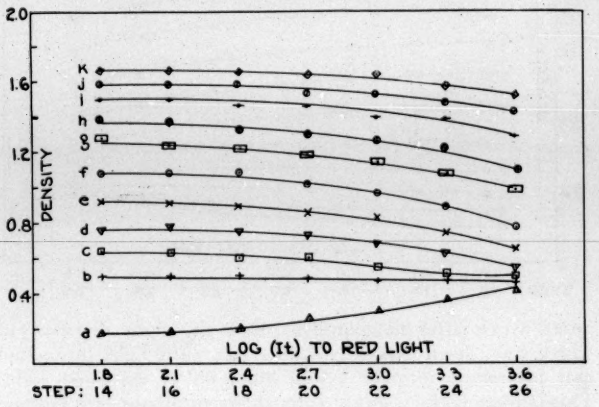
areas which after development have the same density but which have been exposed to different white-light intensities and afterward received equal amounts of infra-red light. This density is the result of three different amounts of energy.

FIG. 16.



Choosing from the H. & D. curves of the original white-light exposures the same 4 densities as with the pure silver bromide emulsion: 0.2, 0.4, 0.9, and 1.5, we get the results indicated

FIG. 17.

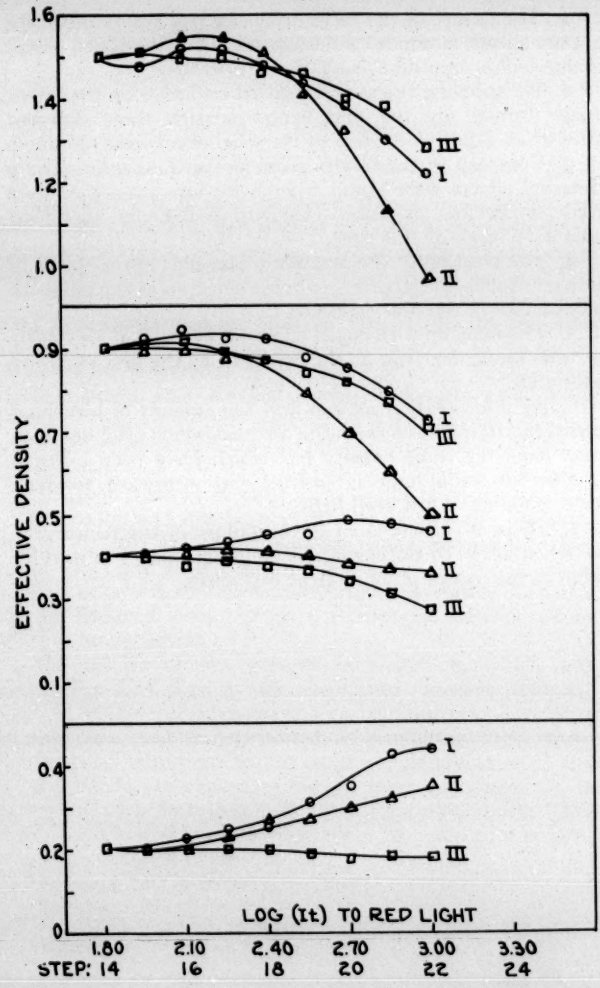


in Fig. 18. Comparing this with Fig. 9 for the pure silver bromide emulsion, we see great differences, especially near the neutral spot. At both densities 0.2 and 0.4 the same differences occur, the greatest effect being at low intensities of the first exposure.

At the density 0.4, the Herschel effect is already marked in the low-intensity exposure, while at the high-intensity exposure no Herschel effect appears. At the optimum intensity the second or infra-red radiation does not seem to change the density. The small deviations in Fig. 18 are all within experimental error.

As shown in this figure the results are in agreement with those on the pure silver bromide emulsion. We observe that the Herschel effect depends on the density and the intensity of the first exposure and the time of the infra-red exposure. The sequence of the effects is otherwise quite different.

FIG. 18.


1.6
1.4
1.2
1.0
III
I
II
0.9
0.7
0.5
0.3
0.1
EFFECTIVE DENSITY
I
III
II
I
II
III
0.4
0.2
0
I
II
III
LOG (It) TO RED LIGHT
1.80
2.10
2.40
2.70
3.00
3.30
STEP: 14
16
18
20
22
24

SUMMARY.

1. The failure of the reciprocity law has been studied for a pure silver bromide emulsion and a super-speed silver bromo-iodide emulsion.

2. By applying the same infra-red radiation on the latent image formed by the first exposure with three different intensities, different degrees of Herschel effect were obtained.

3. Contrary to the results given by W. Leszynski, strong Herschel effects were found when very low intensities were used for the first exposure. General statements, therefore, cannot be made at this time.

4. The position of the maximum Herschel effect shifts, in both emulsions investigated, to lower densities as the intensity is decreased in the first exposure.

5. The maximum Herschel effect for every step also shifts towards lower densities as the intensity of the first exposure is lowered.

6. By interpolation we can find the amount of bleaching caused by the infra-red radiation on areas which after development have the same density but which have been exposed to different white-light intensities and afterward received equal amounts of infra-red light.

7. There is a time effect in the failure of the reciprocity law when infra-red radiation falls on latent images formed by different intensities of white-light exposures.

THE VIBRATION SPECTRUM OF THE AMMONIA MOLECULE.

BY

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University of California at Los Angeles.

THE visible and near infra-red absorption spectrum of gaseous ammonia has been studied by Schierkolk [1] throughout the spectral region 0.6–14.5 μ. It has more recently been examined in greater detail by Sir Robert Robertson and Mr. J. J. Fox [2] between the wave-lengths 1 and 17 μ. There is a good general agreement between the results of the two investigations. Hund [3] has correlated eighteen of the bands observed by Schierkolk on the basis of three fundamental bands, namely, 10.5, 6.1 and 2.22 μ. Using the same data, Hettner [4] has interpreted most of the bands as overtone and combination frequencies of two fundamentals, 10.5 and 6.1 μ. He suggests, however, that a third fundamental may exist near 2.3 μ or possibly at some wave-length beyond 15 μ.

Robertson and Fox have used their own precise measurements to correlate the numerous bands observed. They adopt 10.55 and 6.132 μ as the locations of two fundamental bands, but believe that no simple correlation of all of the bands can be deduced even though a third band be selected as another fundamental.

The results of the present investigation, which was undertaken for a slightly different purpose, however, indicate that the whole near infra-red and visible absorption spectrum of ammonia can be interpreted as originating from three fundamental vibrations within the molecule. The 10.55 and 6.132 μ bands are chosen as two of these fundamentals, in agreement with the selection by the writers cited above. The third fundamental is assumed to occur at 2.916 μ for reasons which are outlined in the following paragraphs.

[1] Schierkolk, *Zeits. für Physik*, **29**, 277, 1924.
[2] Robertson and Fox, *Proc. Roy. Soc. A.*, **120**, 128, 1928.
[3] Hund, *Zeits. für Physik*, **31**, 81, 1925.
[4] Hettner, *Zeits. für Physik*, **31**, 273, 1925.

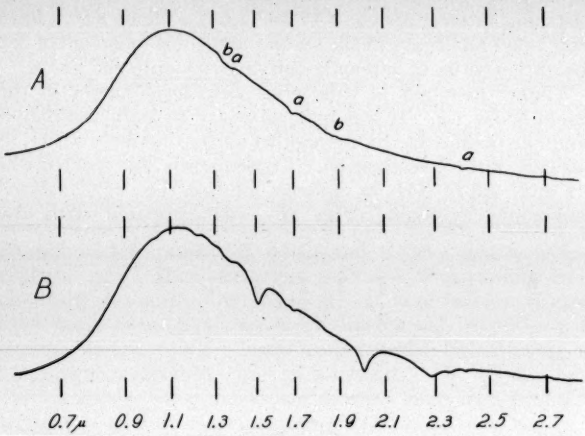
In an investigation of the infra-red absorption spectra of twenty-nine liquid and solid organic derivatives of ammonia it was shown [5] that a series of bands begins at 2.9–3.0 μ and extends with diminishing intensities toward the visible. The frequencies of these absorption maxima obey, at least approximately, the equation of a quantized anharmonic vibrator. Since the bands are strong in the spectra of primary derivatives, considerably diminished in intensity in the secondary derivatives, and absent when the tertiary derivatives are used, the vibrator giving rise to these optical frequencies was sought in the N–H atom pair. The assignment of this series to the N–H bond has been further supported by the results of an attempt made by the writer [6] to evaluate the dissociation energy of the oscillator which gives rise to these frequencies. There is an approximate agreement between the value obtained from the optical data for aniline and the energy computed for a single N–H linkage from chemical data for ammonia.

It was desired to obtain sufficient optical data from the spectrum of the ammonia molecule itself to enable a computation of the energy of an ammonia N–H bond for comparison with that determined thermochemically. It was decided, therefore, to record by means of a registering quartz spectrograph the absorption spectrum of ammonia dissolved in carbon tetrachloride. This solvent was chosen because it is generally reputed to show no absorption bands in the near infra-red. Very slight absorption bands, however, appear in its spectrum even when Eastman's highest purity material is used, as shown in Fig. 1*A*. These are probably caused by CH_2Cl_2 or $CHCl_3$ present as impurities. These bands, marked *a* in the figure, as well as the atmospheric water-vapor bands marked *b*, cause no particular inconvenience in the investigation.

The spectrum of NH_3 in CCl_4 in 3, 15.5 and 78 cm. cells is shown in Figs. 1*B*, 2*A* and 2*B* respectively. Most of the bands which appear are to be found also in the records of Robertson and Fox [2] for gaseous ammonia. The wave-length values are essentially the same, indicating that there is no

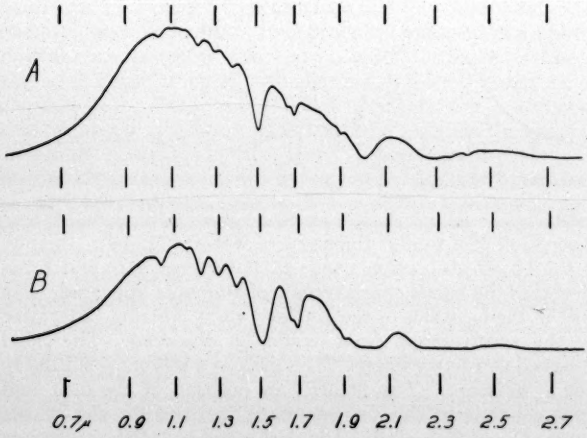
[5] Ellis, *Jl. Amer. Chem. Soc.*, **49**, 347, 1927; **80**, 685, 1928.
[6] Ellis, *Phys. Rev.*, **33**, 27, 1929.

FIG. 1.



A. Absorption by 3.0 cm. of CCl_4. *a*. Impurity bands. *b*. Atmospheric water vapor bands.
B. 3.0 cm. of NH_3 in CCl_4.

FIG. 2.

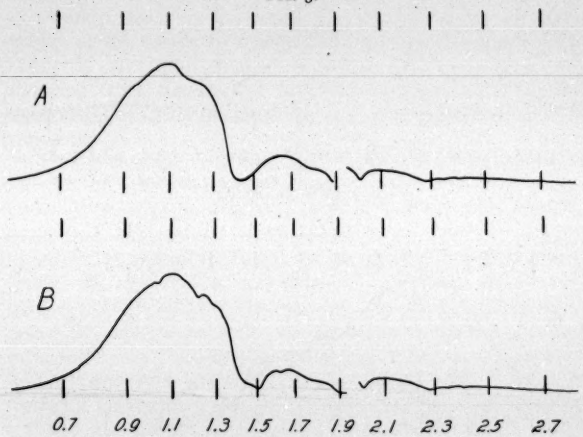


A. 15.5 cm. of NH_3 in CCl_4. *B*. 78 cm. of NH_3 in CCl_4.

appreciable general shift produced by the solvent. Of particular interest are the 1.51 and 1.035 μ bands which have their exact analogues in the second and third members of the absorption series of ammonia derivatives mentioned above.

Higher members of this series were next sought in the region below 1 μ. It was first necessary to learn whether it would be permissible to use another solvent, namely water, in this part of the investigation. Consequently, the spectrum of a 1 mm. cell of NH_3 in aqueous solution, i.e., concentrated ammonium hydroxide, Fig. 3*B*, was compared with the

FIG. 3.



A. 0.1 cm. of water. *B*. 0.1 cm. of concentrated ammonium hydroxide.

absorption of a similar thickness of water, Fig. 3*A*. In spite of the broad absorption bands of water near 1.45 and 1.2 μ, several of the bands characteristic of ammonia appeared. No shift in the locations of the 1.51 and 1.035 μ bands, detectable by the spectrograph used, could be observed. The band observed at 1.655 μ when CCl_4 is used as a solvent is shifted to 1.62 μ, however. The identity in position of the 1.51 and 1.035 μ bands in the two instances justifies the use of the water solvent in a study of higher members of the spectrum

series to which they belong, thus making use of the far greater concentration of ammonia molecules obtainable.

This study of the higher series members was carried out by means of direct photography in a Hilger El quartz spectrograph. A spectrum of a 15.5 cm. cell of concentrated ammonium hydroxide taken on an Eastman "extreme red sensitive" plate revealed a band at $0.795 \pm 0.001\ \mu$, while an exposure through a 78 cm. cell upon a panchromatic plate brought out a band at $0.652 \pm 0.0005\ \mu$. Through the use of a 170 cm. absorbing layer a band appeared at $0.556 \pm 0.001\ \mu$. The two latter bands are not new, having been recorded by Russell and Lapraik [7] at 0.652 and $0.558\ \mu$ nearly a half century ago. They were redetermined here merely as a check on this earlier investigation. It is of interest to note that the $0.652\ \mu$ band remained unchanged in position in Russell and Lapraik's investigation when either ether or ethyl alcohol replaced water as a solvent. The $0.556\ \mu$ band did not appear when the former solvents were used, probably because of a lower concentration of NH_3 molecules.

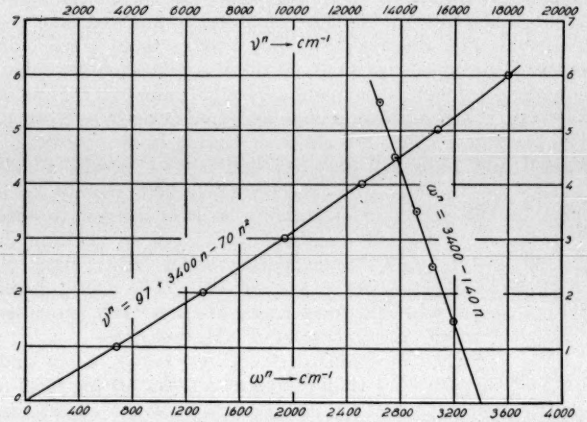
The sequence of bands, 1.51, 1.035, 0.795, 0.652 and $0.556\ \mu$ [8] suggests that they represent a series arising from a fundamental near $2.92\ \mu$. An inspection of the absorption band near $3\ \mu$ recorded by Robertson and Fox clearly indicates that the band is double. It is probably made up of a fundamental with its center near $2.916\ \mu$ and of the first overtone of the $6.132\ \mu$ fundamental with the center of its Q brand at, or near, $2.998\ \mu$. Because of the lack of certainty in locating the exact center of this latter band it will be assigned the value of $3.0\ \mu$ in the discussion of this paper. If one regards the $2.916\ \mu$ band as the first member of a series, the second to sixth members of which are the bands listed at the beginning of this paragraph, and then plots the frequencies of these bands against the integer numbers 1 to 6, the parabolic curve of Fig. 4 results. If first differences, ω'', between successive frequencies are plotted against values of $(n + \frac{1}{2})$ the straight line graph of Fig. 4 results. The intercept on the ω'' axis, ω^0, of this

[7] Russell and Lapraik, *Jl. Chem. Soc.*, 39, 168, 1881.

[8] The constancy in the positions of these bands even when aqueous solution is used may possibly be regarded as evidence supporting the more recent interpretation of ammonium hydroxide as a weak base, that is, that a large portion of the ammonia retains its identity as NH_3 molecules in aqueous solution.

straight line yields $\omega^0 = 3400$ cm.$^{-1}$, while its slope, $2b$, is 140. From considerations of an earlier investigation [6] it was anticipated that the constants of this curve could be substi-

FIG. 4.



Graph of the optical frequencies of the 2.916 μ anharmonic series, ν^n; and of their first differences, ω^n.

tuted into the equation $\nu^n = \omega^0 n - bn^2$ and yield a formula which would express the optical frequencies. It was found, however, that a constant additive term must be included; hence the equation for the optical frequencies turns out to be

$$\nu^n = 97 + 3400n - 70n^2. \qquad (1)$$

The appearance of this constant term is quite unusual. The linear function

$$\omega^n = 3400 - 140n \qquad (2)$$

can be interpreted as expressing in spectroscopic units the actual vibration rates of some anharmonic oscillator within the molecule, which would give rise to optical frequencies

$$\nu^n = 3400n - 70n^2. \qquad (3)$$

The appearance of the 97 cm.$^{-1}$ term in the equation expressing the optical frequencies may be explained as follows. Suppose

the energies in the nth and n'th stationary states of the oscillator whose vibration rates are the ω^n values of Eq. (2) are expressible by

$$E^n = hc_1 + h\omega^0 n - hbn^2, \tag{4}$$

$$E^{n'} = hc_2 + h\omega^0 n' - hbn'^2. \tag{5}$$

The optical absorption frequencies which would arise in the typical infra-red case, for which $n' = 0$, would be [9]

$$\nu^n = \frac{E^n - E^{n'}}{h} = (c_1 - c_2) + \omega^0 n - bn^2. \tag{6}$$

The constant energy difference term $h(c_1 - c_2)$ which gives rise to the constant optical term $(c_1 - c_2)$ may be explained on the assumption that a slight additional amount of energy is absorbed before, or while, absorption by vibration takes place. Although it is much smaller, this term is of the nature of an electronic energy change. Possibly it represents a slight increase in molecular potential energy caused by a slight inter-nuclear rearrangement.

In the earlier investigation [6] referred to it is possible that in some instances a small constant term should be added to the optical equations as given; however, the accuracy of the ω^n data is hardly sufficient to permit a decision on this question in those instances.

On the assumption that the $(3400n - 70n^2)$ portion of Eq. (1) arises from an anharmonic oscillator within the molecule, the dissociation energy D of the oscillator may be calculated by the method devised by Birge and Sponer [10] for homopolar, diatomic, gaseous molecules and adopted by the writer [6] in the approximate evaluation of the heats of linkage of C–H and N–H bonds. This value may be computed in calories per mole from the following equation:

$$D = hc(\omega^0)^2 N/4bJ, \tag{7}$$

where h is Planck's constant, c the velocity of light, N the Avogadro number and J the mechanical equivalent of heat

[9] If $(n + \frac{1}{2})$ and $(n' + \frac{1}{2})$ were used in place of n and n' in Eqs. (4) and (5), as required by wave mechanics, the only change introduced into Eq. (6) would be in the interpretation of the coefficient of the linear term in n.

[10] Birge and Sponer, *Phys. Rev.*, **28**, 259, 1926.

in ergs per calorie. If the values of these constants and the values of ω^0 and b obtained from Fig. 4 are substituted in Eq. (7), D evaluates as 118,000 cal./mole, or 5.1 equivalent volts.

Now the average energy required to remove a hydrogen atom from an ammonia molecule can be approximated by taking one-third of the sum obtained from the addition of the heat of formation of NH_3, one-half of the heat of dissociation of N_2 and three-halves of the heat of dissociation of H_2. The values in calories per mole used here for these energies are as follows: 12,000,[11] 214,500 [12] and 102,000.[13] The value for the dissociation energy computed in this manner is

$$D = \tfrac{1}{3}(12{,}000 + \tfrac{1}{2} \times 214{,}500 + \tfrac{3}{2} \times 102{,}000) = 92{,}000 \text{ cal./mole}$$

or 3.99 equivalent volts.

The general agreement between the two values, 5.1 and 3.99 volts, is believed to be sufficient to justify an identification of the N–H bond as the source of the oscillations. 3.99 volts measures the average energy required to remove the three hydrogen atoms in turn from the nitrogen atom, and this may differ appreciably from the energy which the optical method is interpreted as revealing. Again, the method underlying the optical determination rests upon a long extrapolation of the $\omega^n : n$ curve of Fig. 4. There is no assurance that this curve remains linear over this extrapolated region in this instance. On the contrary, there are numerous examples of considerable deviation from linearity in the application of this method to diatomic molecules, in which the curve can be carried through much larger values of n. It is not infrequent in such cases that errors of the order of magnitude of the difference between the 5.1 and 3.99 volt values are introduced by long extrapolations. Of particular interest in this connection is the failure of the extrapolation of the frequencies associated with the normal nitrogen molecule. The early value for the heat of dissociation obtained in this manner by Birge and Sponer [10] was 11.4 volts, whereas the

[11] Landolt-Börnstein Tables.

[12] Herzberg, *Ann. der Physik*, **86**, 189, 1928; Birge, *Nature*, **122**, 842, 1928; Mulliken, *Nature*, **122**, 842, 1928; Kaplan, *Phys. Rev.*, **33**, 267, 1929. The value adopted is the average of the 9.1–9.5 volt values given by these investigators.

[13] Birge, *Nature*, **121**, 134, 1928.

value now accepted is around 9.3 volts.[12] This represents an error of nearly 23 per cent. arising from a linear extrapolation of the $\omega^n : n$ curve. This is quite comparable to the apparent 28 per cent. failure in the value determined above for the N–H bond.

In Table I are assembled the wave-lengths of the ammonia bands as measured by Robertson and Fox,[2] Schierkolk [1] and the writer. In the fifth column is given the interpretation of these bands in terms of the three fundamentals, 10.55, 6.132 and 2.916 μ, these values being taken from the measurements by Robertson and Fox. The subscript refers to the fundamental while the superscript designates the overtone involved, the first overtone having the superscript 2. Column 4 lists the values of the wave-lengths calculated according to column 5.

TABLE I.

Absorption Bands of Ammonia.

Robertson and Fox.	Schierkolk.	Ellis.	Calculated.	Interpretation.
10.55 μ	10.315 μ	—	—	ν_1^1
6.132	6.136	—	—	ν_2^1
4.05	3.896	—	3.88 μ / 4.02	$\nu_1^1 + \nu_2^1$ / $\nu_3^1 - \nu_1^1$
2.916	2.974	—	—	ν_3^1
2.0	2.974	—	—	ν_2^2
—	—	2.35 μ	2.34	$\nu_1^1 + \nu_2^2$
2.264	2.239	2.28	2.285	$\nu_1^1 + \nu_2^1$
1.967	1.935	2.01	1.975	$\nu_2^1 + \nu_3^1$ / ν_3^2
1.663	1.643	1.655 ‡	1.665	$\nu_1^1 + \nu_2^1 + \nu_3^1$
1.513	1.493	1.51	1.51 *	ν_3^2
—	—	1.46	—	ν_2^4
1.307	1.298	1.29	1.32	$\nu_1^1 + \nu_3^2$
1.212	1.20	1.21	1.21	$\nu_2^1 + \nu_3^2$
1.023	1.016	1.035	1.035 *	ν_3^3
—	0.916	—	0.945	$\nu_1^1 + \nu_3^3$
—	—	0.795	0.795 *	ν_2^4
—	0.736	0.733	0.739	$\nu_1^1 + \nu_2^4$
0.652 †	— / 0.613	0.652	0.652 *	ν_3^5
0.558 †	—	0.556	0.556 *	ν_3^6

* Calculated from Eq. 1.

† Measurements by Russell and Lapraik.[7]

‡ 1.62 μ when water is used as a solvent.

It appears that the 10.55 μ band has no overtones. There is evidence which indicates that the 6.132 μ fundamental has overtones, the frequencies of which are slightly greater than even multiples of the fundamental frequency. Thus the overlapping band near 3.0 μ and the band near 1.46 μ, manifest through a slight inflection in the side of the strong 1.51 μ band, are interpreted as first and third overtones of the 6.132 μ fundamental. This type of non-harmonic series is not typical but should not be considered improbable so long as the nature of the vibrator is not known.

One difference band probably is present. The 4.02 μ absorption band which would arise from a simultaneous positive change in the 10.55 μ vibration and a negative change in the 2.916 μ vibration agrees well with the weak band observed by Robertson and Fox at 4.05 μ and by Schierkolk at 3.896 μ. However, absorption in this region may be partly due to a $(\nu_1^1 + \nu_2^1)$ band. The appearance of a weak difference band associated with the 10.55 μ band is not surprising in view of the appearance of "anti-Stokes" lines in the Raman effect corresponding to infra-red wave-lengths in this region of the spectrum. The presence of lines of the anti-Stokes type means that even at room temperatures the incident frequency finds a portion of the molecules already in possession of vibratory energy, which they give over to the incident quantum during the scattering process. Thus Raman and Krishnan [14] have found this type of modified line associated with a wave-length as low as the 10.1 μ absorption band of benzene.

The locations of some of the combination bands seem to depend upon the solvent. Thus the 1.655 μ band observed with CCl_4 as a solvent appears at 1.62 μ when water is used. Probably the shift of the 1.97 μ band of ammonia gas to 2.01 μ when the former solvent is used is caused by the presence of the solvent. Again $(\nu_1^1 + \nu_3^4)$ appears at 0.733 μ instead of at its calculated wave-length of 0.739 μ. These shifts doubtless indicate actual changes in the positions of the longer wave-length fundamentals. It is important, however, in connection with this investigation that the overtones of the 2.916 μ band apparently are not appreciably affected by the solvent.

[14] Raman and Krishnan, *Indian Jl. Phys.*, **2**, 399, 1928.

The absorption spectra of the amines [5] are of interest in connection with this study, not only because anharmonic series of bands appear, corresponding to the 2.916 μ series of NH_3, but also because of the presence of bands at 2.01–2.10 μ and 1.21–1.23 μ. The writer [5] has already interpreted these latter bands in a manner similar to the interpretation of the 1.97 and 1.21 μ bands of ammonia, namely, as frequencies arising from combinations of a fundamental band near 6.2 μ and a fundamental near 3 μ and its first overtone near 1.5 μ respectively. Much evidence for the existence of a 6.2 μ fundamental in the spectra of primary ammonia derivatives is found in the spectra recorded by Bell, especially in his spectra of primary alkyl amines [15] and this evidence has been pointed out by that author. The 6.2 μ band is obviously absent in the spectra of the secondary alkyl amines. If the weaker band at 2.10 μ found in the writer's short wave-length records of the secondary amines really corresponds to the 2.01 μ band of the mono-derivatives, one would expect to find the 6.2 μ fundamental shifted to 6.8 μ. It would be difficult to determine its presence at that position, however, because a strong hydrocarbon band exists there.

The apparent presence of a 6.2 μ fundamental band in the spectra of ammonia derivatives suggests that the origin of this band may also be in the N–H pair. Possibly it arises from a vibration of the hydrogen atom at right angles to the inter-nuclear line. Such a type of vibration has been assumed and discussed in other instances both by Salant [16] and by Andrews and Haworth.[17]

Whatever the origins of the 6.132 and the 2.916 μ bands of ammonia are, and in general of the 6 and 3 μ bands of the amines, it is the author's belief that there are cases parallel to this in the spectra of other molecules. In the spectra of hydrocarbons, for example, there are apparently at least two fundamental bands at 3.2–3.5 μ and 6.6–7.7 μ respectively which arise from the C–H atom pair. The bands found by Robertson and Fox in the spectra of PH_3 and AsH_3 and designated by them as I and II (wave-lengths at 8.889 and 4.297 μ for phosphine and at 9.946 and 4.713 μ for arsine)

[15] Bell, *Jl. Amer. Chem. Soc.*, **49**, 1837, 1927.
[16] Salant, *Proc. Nat. Acad. Sci.*, **12**, 334 and 370, 1926.
[17] Andrews and Haworth, *Jl. Amer. Chem. Soc.*, **50**, 2998, 1928.

probably are not a fundamental and its overtone, but rather two distinct fundamentals, quite analogous to the 6.132 and 2.916 μ bands of NH_3.

The variations in the wave-length positions of the members of the 2.9 μ series of ammonia when one hydrogen atom is replaced by an organic radical is of interest. Consider, for example, the first overtone. The 1.51 μ band of NH_3 shifts to 1.50 μ and 1.55 μ for $NH_2.C_6H_5$ and $NH_2.C_5H_{11}$ respectively. The shift to 1.55 μ when the saturated amyl radical is substituted is believed to be largely the result of an increase in the mass of the vibrator, assuming the H atom to vibrate against the ($NH.C_5H_{11}$) radical. The shift from 1.55 μ back to 1.50 μ when the C_6H_5 phenyl radical is substituted is believed to be due largely to the greater tightness of the hydrogen-phenyl bond. There is probably a complete analogy to these shifts in the 1.69, 1.68 and 1.74 μ bands of methane, benzene and hexane molecules respectively. These bands are assumed to arise from anharmonic vibrations of the following oscillators: CH_3–H, C_6H_5–H and C_6H_{13}–H.

SUMMARY.

1. The infra-red absorption spectrum of ammonia in carbon tetrachloride and aqueous solutions has been studied with a registering quartz spectrograph. The visible spectrum in aqueous solution has also been examined with a Hilger El spectrograph.

2. The absorption bands obtained are quite analogous to those usually observed with ammonia gas. The positions of certain of the bands depend upon the solvent while others do not.

3. Of particular interest is a series of bands, 2.916, 1.51, 1.035, 0.795, 0.652 and 0.556 μ, whose positions are apparently independent of the presence or nature of the solvent. The frequencies of these bands obey the equation: $\nu^n = 97 + 3400n - 70n^2$. They are believed to arise from anharmonic vibrations within the N–H bond for the following two reasons:

a. The energy of the oscillator, 5.1 equivalent volts, calculated from the above equation agrees approximately with the energy of a single N–H linkage, 3.99 equivalent volts, computed chemically.

b. This series of bands persists, with systematic minor shifts, in the spectra of primary and secondary organic derivatives of ammonia.

4. The appearance of the constant term, 97 cm.$^{-1}$, in the equation is unusual. It is interpreted as arising from a change in potential energy of the molecule, before or while absorption by vibration takes place, arising from a slight inter-nuclear rearrangement.

5. The whole infra-red and visible vibration spectrum of the NH_3 molecule can be correlated on the basis of three fundamental bands, 10.55, 6.132 and 2.916 μ.

6. The second, as well as the last, of these bands is believed to be associated with the N–H bond, inasmuch as it persists in the spectra of many of the organic derivatives of ammonia. It possibly has non-harmonic overtones of a positive deviation type.

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Total Reflection of X-Rays from Nickel Films. H. W. EDWARDS. (*Phys. Rev.*, April, 1929.) In the early days of X-rays all attempts to show that they possessed the properties of light met with failure. In contrast with that time we are now convinced by experiment that they are refracted, totally reflected and diffracted as is visible light. The author of this paper has already investigated for nickel films the critical angle of the wave-length .707 Å. He sputtered the metal films upon glass as a support. He found that the value of the critical angle increased with increasing thickness of the film. It rose from .0016 radians for glass alone to more than twice as much for the thickest film. "The final value agreed with that calculated by the Lorentz dispersion formula, assuming a density of 8.75 for nickel. The increasing value of the critical angle with increasing thickness of the nickel was taken as evidence for supposing that the electrons of the underlying glass support participated in the phenomenon of reflection and gave values for the critical angles which might have been construed as due to abnormally small values of the density of the nickel." To further study the relation of thickness of film to critical angle the investigation reported in this paper was undertaken. Eight platinum films were prepared by sputtering upon as many pieces of glass cut from the same sheet. The duration, voltage, gas pressure and distance from cathode to glass was kept the same in all the operations. The platinum film was opaque to intense light and showed the same critical angle for X-rays as a much thicker film. Subsequently upon seven of the platinum films were sputtered nickel films whose thicknesses were different because the deposition had different durations ranging from 2 to 50 min. From the thinnest film onward their colors were white, light yellow, yellow orange, purple, blue white, white. The critical angles for the several thicknesses of nickel are as follows:

Thickness in 10^{-8} cm.	0.00	0.08	0.12	0.16	0.205	0.25	0.41	2.05
Critical angle in radians	0.0040	0.0043	0.0043	0.0043	0.0041	0.0039	0.0037	0.0034

Value calculated from dispersion theory 0.0034.

The critical angle for the thickest film on glass was the same as for the thickest film on platinum. The four thinnest films on platinum showed greater critical angles than the platinum alone. "These results would seem to indicate that the electronic density of the combined metals is greater than that of either the nickel or platinum alone. If this is the case one would expect that the first nickel atoms deposited upon the platinum are embedded among the platinum atoms producing an alloy having a greater density than the platinum alone. The fact that the nickel films adhere tenaciously to the platinum films supports this view-point."

G. F. S.

VELOCITY AND ACCELERATION OF ARROWS. WEIGHT AND EFFICIENCY OF BOWS AS AFFECTED BY BACKING OF BOW.

BY

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INTRODUCTION.

HAVING taken up archery as a means of obtaining recreation, and being a research physicist, I naturally became very much interested in many of the physical problems associated with this science.

I have investigated many of these problems, both mathematically and experimentally. The results have been surprising and interesting. One of these problems which has been investigated is the effect of the bow backing on the velocity and acceleration of arrows, and on the weight and efficiency of the bow.

This investigation was prompted by the fact that I am not physically strong enough to use heavy bows. The efficiency of the bow is a very vital factor to those of us who are obliged to use relatively weak bows.

It has long been the custom not only among civilized nations, but even among the savage tribes, to place some sort of backing on the bow, in order to decrease the probability of breaking it. Many substances have been used such as raw hide, sinew, hickory, etc.

While I was, of course, interested in preventing the bow from fracturing, at the same time I did not want to sacrifice the efficiency of the bow by using a backing. With this thought in mind, I began a series of tests to determine the effect on the efficiency of the bow of using different types of backing. The method, in brief, consisted of weighing the bow (i.e. determining the force required to draw it) and then shooting arrows of different weights with it, using a mechanical shooting device to hold the bow. The velocities of arrows discharged from the bow were accurately determined and

from these data the efficiency of the bow was obtained. Various types of bows with different types of backing were tested.

The tests were carried out in the Research Laboratory of the American Piano Company. The fiber-backed bows were furnished by Mr. Phillip Rounsevelle of the Archers Company, Pinehurst, North Carolina.

Shooting device showing electric contacts.

METHOD OF CONDUCTING TESTS.

It was realized that in order to obtain results that could be reproduced at will, it would be necessary to mount the bow in a mechanical shooting device. I had previously designed such a device for testing arrows. This mechanical shooter is made in such a manner that it practically duplicates the conditions obtained in shooting by hand. The arm on which the bow is mounted is free to pivot in a manner exactly like the human arm. The fingers which grasp the string are locked into position by means of a trigger. The trigger

is released pneumatically. In this manner there is no danger of disturbing the mechanism at the time the trigger is released. With this device, using good arrows, it is possible to obtain "golds" consistently at 50 to 60 yards.

A device of this type was equipped with a series of electrical contacts, so placed that they were closed by a silver pin on the arrow as it was leaving the bow. There was a sufficient number of these contacts to plot a space time curve from the chronograph readings.

The chronograph used was a modification of the Aberdeen chronograph developed during the war. This chronograph was modified and improved by the Ampico Research Laboratory. It was used in these tests and gave results that were very satisfactory. In addition to the space time curves which were plotted from the chronograph readings, the velocity of the arrow at the time it left the bow was also further checked by shooting the arrow through tin foil screens which were two feet distant from each other. The accompanying photograph shows a "set up" in the laboratory used in making these measurements.

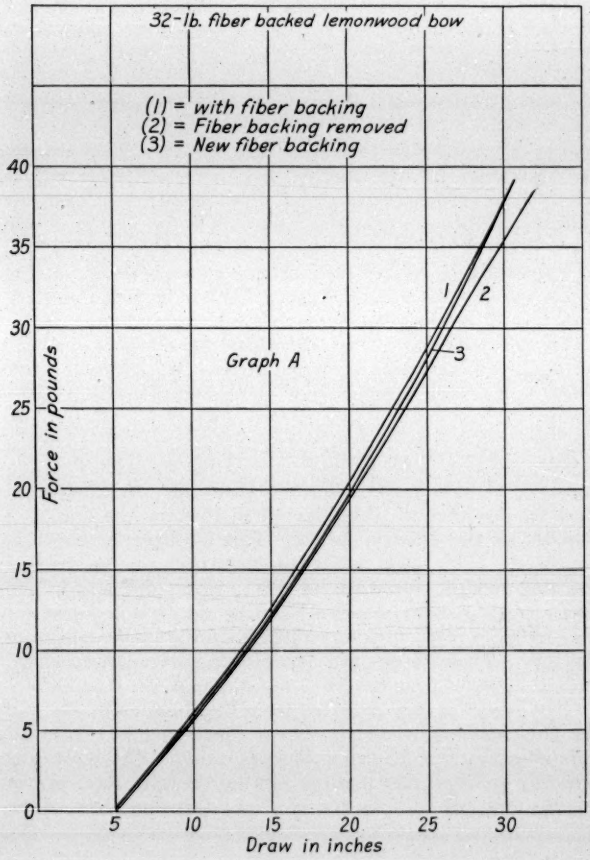
Since it was desirable to determine the effect of shooting arrows of different weight, four different weights were used. These arrows weighed 230, 365, 545, and 635 grains, respectively.

The first bow which was tested was a 32 lb. fiber backed lemonwood bow, which was furnished by the Archers Company. The bow was carefully weighed and a curve plotted showing the force in pounds required to draw the bow as a function of the draw in inches. This is shown by curve 1, Graph *A*. This bow was then placed in the mechanical shooting device, and each of the arrows discharged, and chronograph records obtained showing the time required for the arrows to reach various positions, during their flight from the bow. From these data, space time curves were plotted and are shown by curves No. 1 in Graphs *B*, *D*, *F* and *H*.

The bow was now removed from the shooting device and the fiber backing removed. Great care was taken to avoid removing any wood during this operation. This bow was carefully weighed and a curve plotted showing the force in pounds required to draw the bow as a function of the draw

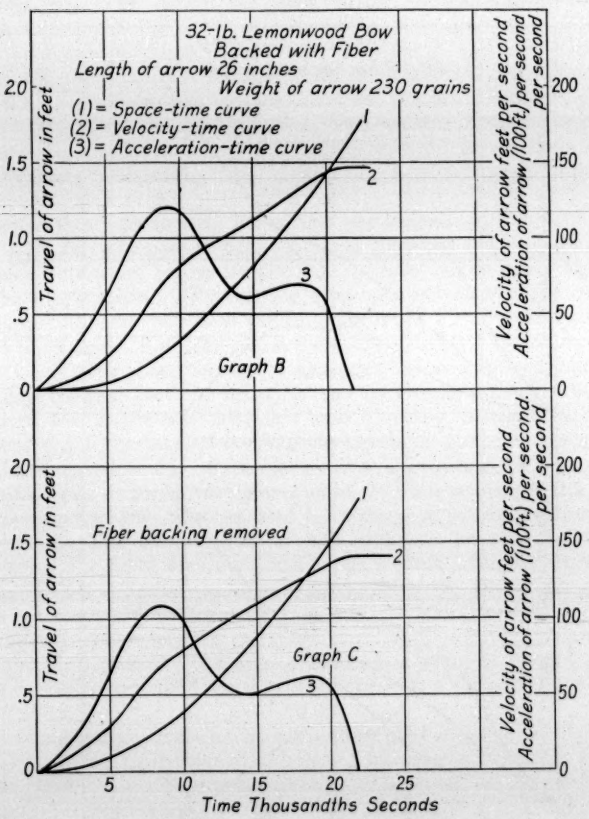
in inches. See curve 2, Graph *A*. The bow was then replaced in the shooting device and the arrows again discharged, obtaining, as before, chronograph records from which space time curves were plotted. These curves are reproduced by No. 1, in Graphs *C*, *E*, *G* and *I*.

GRAPH *A*.



All of the No. 1 curves of Graphs *B* to *I* inclusive were now graphically differentiated. The space time curves were drawn on large sheets 17 x 22 inches, and the graphical differentiation carefully performed. The velocity time curves

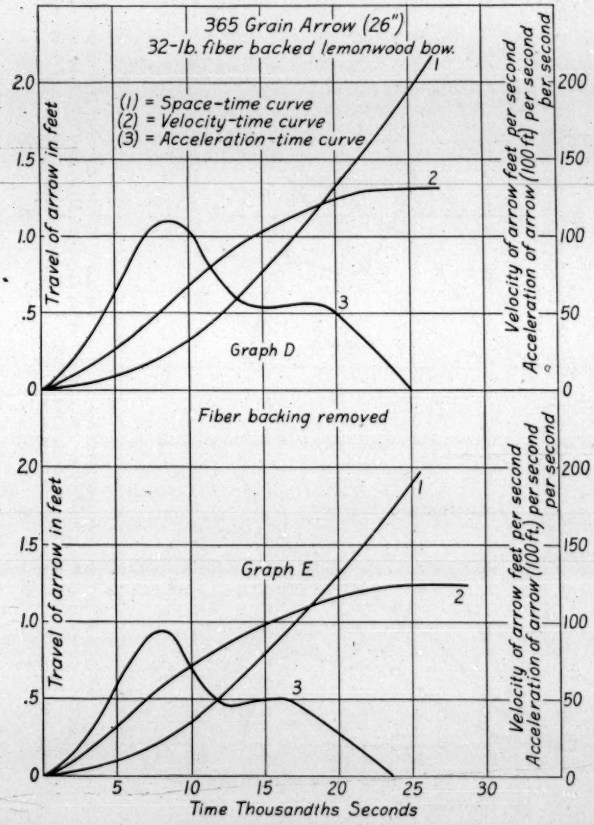
GRAPH *B*.
GRAPH *C*.



which were obtained from this differentiation were then plotted on the same sheet and are shown by the curves No. 2 in Graphs *B* to *I* inclusive.

The velocity time curves were then graphically differenti-

GRAPH *D*.
GRAPH *E*.



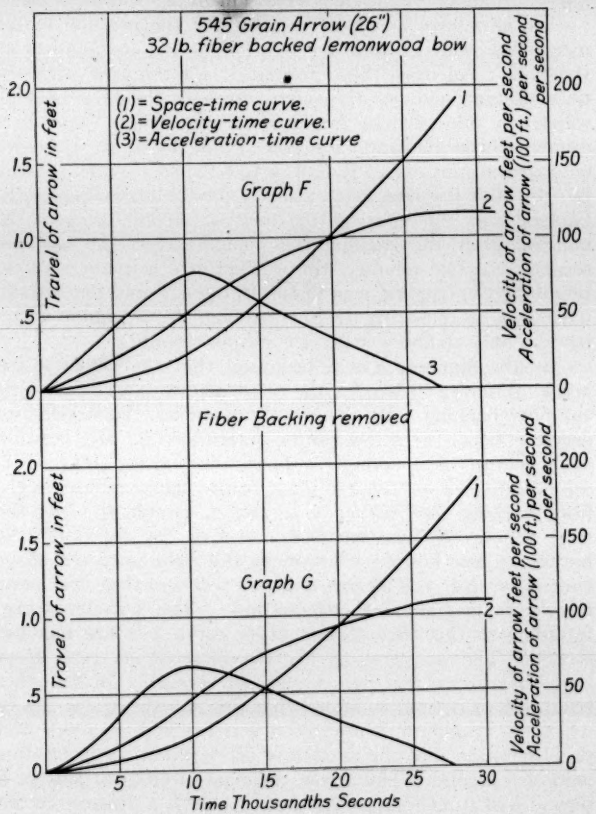
ated and the acceleration time curves obtained and plotted. These are shown by the curves No. 3 in graphs *B* to *I* inclusive.

We now have a complete history of the position of the arrow, its velocity, and acceleration during its flight from the bow. We have this information for the bow with the fiber backing, and for the same bow with the fiber backing removed. The curves for each arrow, before and after removing the backing, are placed on the same page for comparison purposes. Referring to Graphs *B* and *C*, it will be seen that the maximum velocity for the arrow before the backing was removed was 147 feet per second, whereas the velocity after the backing was removed was 140 feet per second. In like manner, the maximum acceleration before removing the backing was 12,000 feet per second per second, whereas after removing the fiber backing the maximum velocity was only 10,800 feet per second per second.

In like manner, it will be found that the velocity and acceleration are higher for the other arrows before removing the fiber backing. By reading these curves, the velocity or acceleration of the arrow can be determined for any position of the arrow. For example, suppose the velocity and acceleration is desired for the 230 grain arrow before removing the fiber backing (see curves 1, 2 and 3, Graph *B*). At the time the arrow has travelled one foot, by following the horizontal line labeled 1.0 foot, to the right until the space time curve No. 1 is intersected, you will find that the arrow has been in flight for .167 second. The velocity corresponding to this time as read from curve 2 is 122 feet per second. The acceleration at this moment as read from curve 3 is 6,700 feet per second per second. On the other hand, if it is desired to know what position the arrow was in when the maximum acceleration was reached, you will find this by noting that the maximum acceleration occurred after .009 of a second. The arrow, after an interval of .009 of a second had travelled, as read from curve 1, a distance of .25 of a foot.

In archery, we are particularly concerned with the velocity of the arrow as it leaves the bow. This velocity (or what is known in ballistics as muzzle velocity) is shown by the maximum height reached by curves No. 2 in Graphs *B* to *I* inclu-

GRAPH *F*.
GRAPH *G*.



sive. The maximum velocities were taken from these curves and plotted on Graph *J*. This gives us curve No. 1, which shows the velocities of the various weight arrows at the time they left the string for the bow with the fiber backing. Curve No. 2 on the same graph shows these velocities for the same bow with the fiber removed.

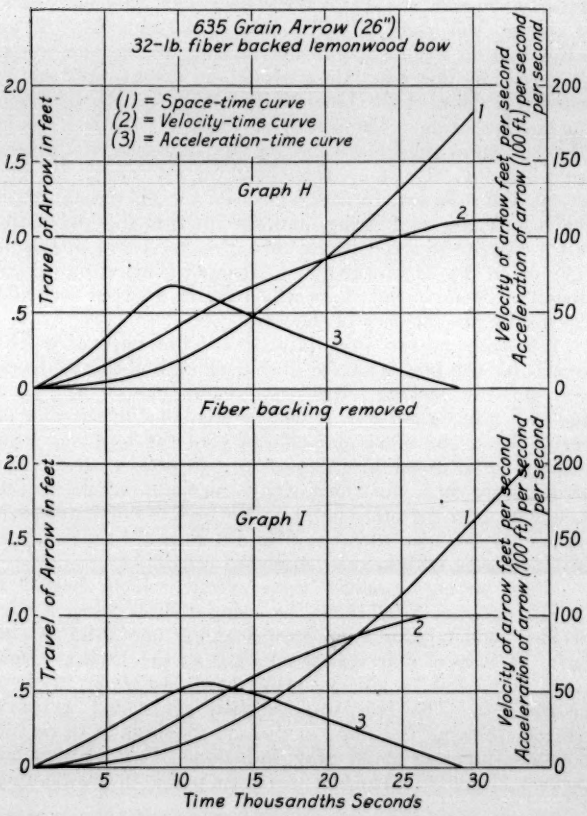
By integrating curves 1 and 2 of Graph *A*, the total input in foot pounds of work may be obtained. Also, since the kinetic energy of the arrow as it leaves the bow is equal to $MV^2/2$, where M is the mass of the arrow, and V its velocity, we can determine the energy or the amount of work that the arrow is capable of doing. Dividing this work which the arrow is capable of doing by the work done in drawing the bow, we obtain the efficiency of the bow. This, of course, will vary with the weight of the arrow. If an arrow had no weight at all, the efficiency of the bow would be zero. In this case, there would be energy used up in internal friction of the bow, air resistance on the bow and the moving string. The rest of the energy of the bow would be taken up at the time the string stops the ends of the bow from moving. On the other hand, if the arrow is very heavy, the only loss in energy will be the air resistance on the bow, arrow and string, and the internal friction of the bow. When the arrow leaves the string there will be practically no energy left in the bow. Arrows having intermediate weights will have efficiencies which are in between zero and the maximum efficiency of the bow.

Efficiency curves were plotted for the various weight arrows for the bow with the fiber backing and for the same bow without backing. These curves are shown as No. 1 and No. 2 in Graph *K*. It will be seen that in the case of curve No. 2 the maximum efficiency of the bow has been reached in an arrow weighing about 650 grains. If heavier arrows were shot, this curve would continue parallel to the base line. On the other hand, in the case of curve 1, which represents the bow with the fiber backing, the efficiency is still increasing with increase in arrow weight.

After having obtained these results which showed a decided increase in efficiency by using fiber backing, it was decided to determine the effect of gluing new fiber on the bow. A strip of fiber was obtained from the Archers Company and carefully glued to the bow, according to their instructions. The bow was weighed again and a curve plotted, showing the force in pounds required to draw the bow as a function of the draw in inches. This is shown by curve 3, Graph *A*. The bow was again placed in the shooting

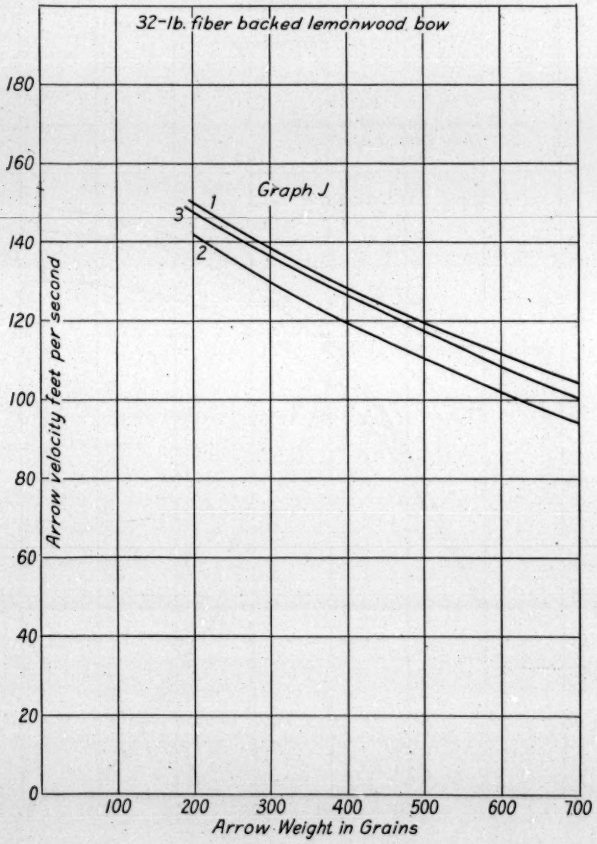
device and space time curves plotted from the chronograph readings as explained before. These curves were graphically differentiated, obtaining velocity time curves and acceleration time curves. All of these curves were so nearly like those shown in Graphs *B*, *D*, *F* and *H*, that they are not reproduced

GRAPH *H*.
GRAPH *I*.


635 Grain Arrow (26")
32-lb. fiber backed lemonwood bow
(1) = Space-time curve
(2) = Velocity-time curve
(3) = Acceleration-time curve
Graph H
Travel of Arrow in feet
Velocity of arrow feet per second
Acceleration of arrow (100 ft.) per second per second
Fiber backing removed
Graph I
Time Thousandths Seconds

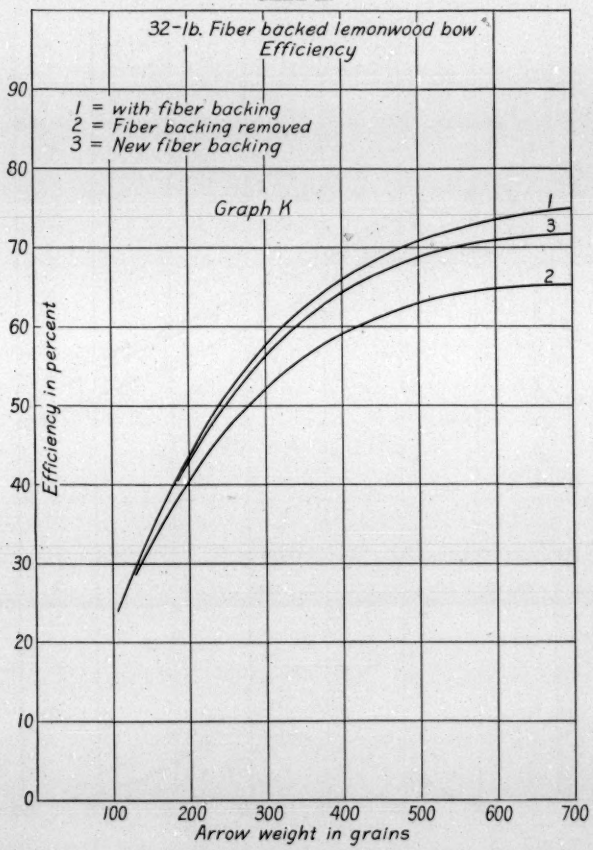
here. The velocity curve was drawn showing the velocity as a function of the arrow weight. This is shown by curve 3, Graph *J*. The efficiency curve was also drawn and is shown by curve 3, Graph *K*. It will be seen that the new fiber as placed on the bow brought the efficiency back almost to

GRAPH *J*.



where it was in the beginning. The slight discrepancy which does exist was due no doubt to the fact that the bow had, by long use, taken a permanent set, or, as expressed by the archer, it had "followed the string." In gluing the new fiber on, this curvature was followed so that the fiber was

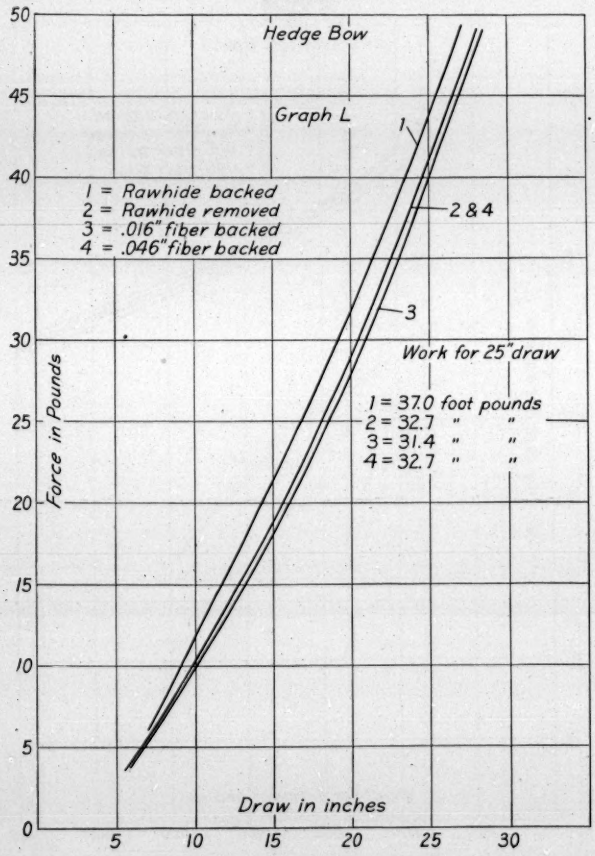
GRAPH K.



not under as much tension as the original fiber which was glued on before the bow had ever been drawn.

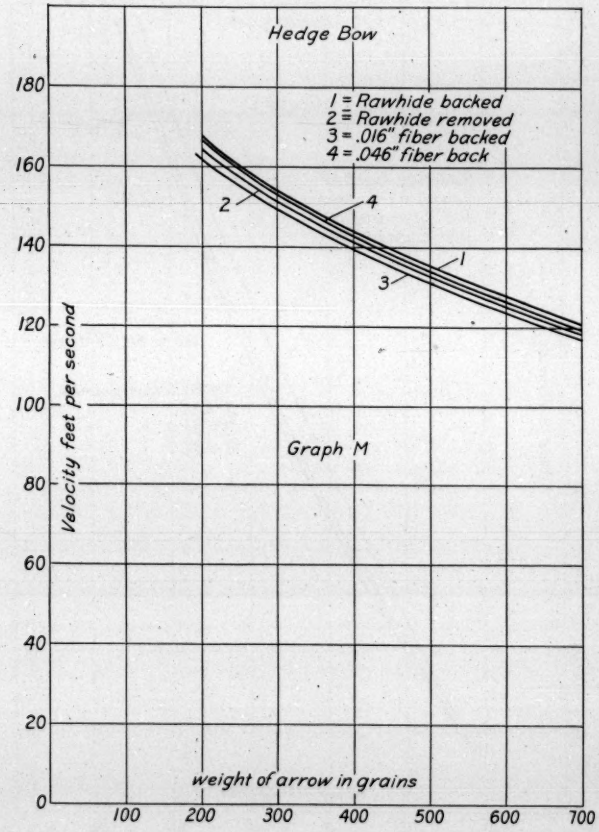
After having obtained the foregoing results, which were not only interesting, but surprising, I decided to test the effect of backing a bow with raw hide. For this test, I used

GRAPH L.



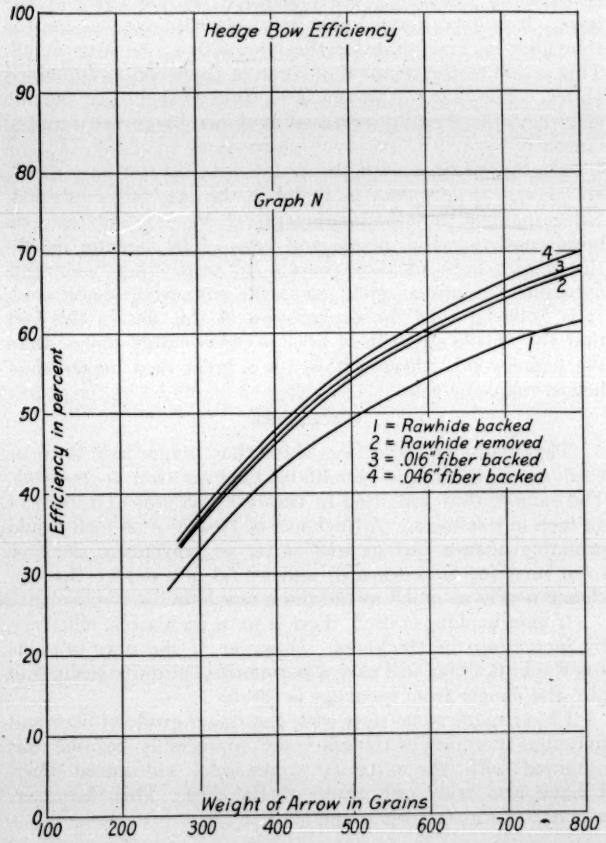
an Osage bow backed with raw hide. The bow was subjected to the same tests as the lemonwood bow. The space time, velocity time and acceleration time curves are not reproduced in this paper, but the weight of the bow, the velocity of the arrow, and the efficiency of the bow are shown by curves 1,

GRAPH *M*.



Graphs *L*, *M* and *N*. The raw hide was removed from the bow and another set of curves obtained as shown by curves 2 in Graphs *L*, *M* and *N*. The bow was then backed with fiber, which was .016″ in thickness. Before gluing this fiber in place, it was necessary to remove some of the wood from

GRAPH *N*.



the back of the bow in order to obtain a smooth surface. Curves 3, Graphs *L*, *M* and *N*, show the results obtained with the bow in this condition. This thin fiber was now removed and fiber which was .046" thick substituted. Curves 4 in Graphs *L*, *M* and *N* show the results under this condition. It will readily be seen by comparing curves 1 and 2 Graph *N* that the raw hide greatly reduced the efficiency of the bow. It will be noticed that the velocities are less for the thin fiber backing than for the bow with no backing at all. This is due to the removal of some of the wood as explained above. The bow was at the same time weakened so that its efficiency was actually increased as shown by curves 2 and 3, Graph *N*.

The use of fiber with the hedge bow did not give as big an increase in efficiency as it did in the case of lemonwood. Since making these measurements, I have made tests on bows constructed of maple and yew. The increase in efficiency with both of these woods by using fiber backing is apparent but not as great as is the case with lemonwood. It is believed that the explanation of this lies in the fact that the tensile strength of fiber is considerably higher than the lemonwood, whereas it is not a great deal higher than hedge, maple or yew.

CONCLUSIONS.

The results of these tests show that if raw hide is to be used as a backing, it should be kept as thin as possible. The sample that was used in the test was almost 1/16th of an inch in thickness. A thickness of 1/64th of an inch would probably answer just as well as far as preventing the bow from breaking is concerned, and would not reduce the efficiency nearly so much as the thick raw hide.

If fiber backing is used, there is some increase in efficiency by increasing the thickness. However, if the fiber is made too thick, the bow will take a permanent set quite easily and also the danger from breakage is greater.

I have made some tests with a stronger grade of fiber and find that it improves the efficiency appreciably beyond that obtained with the ordinary commercial vulcanized fiber. I have also tried one grade of Bakelite. This, however, was not as satisfactory as the fiber.

On first thought, anyone might reach the conclusion, after seeing these curves, that since the velocity of the arrow is only increased about 5 to 6 per cent. by using fiber backing that the results are hardly worth while. However, it should be remembered that the increase in energy is proportional to the square of the velocity so that the actual increase in energy is from 10 to 12 per cent. In like manner, the actual increase in the efficiency of the bow, as shown by the curves, is from 8 to 14 per cent., depending upon the weight of the arrow that is being used.

The same thing is true with raw hide except in the reverse order. The decrease in efficiency due to the raw hide backing amounts to about $8\frac{1}{2}$ per cent.

Judging by the general shape of the acceleration curve for all of the various bows which have been tested in the laboratory, it is believed that there is an opportunity of further increasing the efficiency of a bow by changing its design. The acceleration curves are too steep at the beginning and do not hold up well enough toward the end. It is believed that this condition can be improved.

Study of Snow Handling Methods Needed. *Public Works*, Aug. 1929. The total annual depths of snowfall reported by thirty-six snow removal states, and even by different parts of the same state, differ greatly. California reports one inch minimum annual fall for the southern part of the state and 783 inches as the maximum in the northern part. Delaware reports 16.7 inches as its minimum and 22.9 as its maximum.

While it may not be impossible to keep open mountain roads where 65 feet of snow falls in one season, it is evident that the methods and equipment employed must be vastly different from those found satisfactory in Delaware. Different states have necessarily developed different methods; but while some have paid little attention to the methods developed in others, a few states have copied methods found satisfactory elsewhere without sufficient regard for the different conditions. Either is of course wrong; but the former is preferable, for it will secure progress and the ultimate evolution of the best plan for each class of conditions.

The problem is a new one, but the point has been reached where officials of all the snow states should get together and compare methods and develop a science of snow handling whereby the most effective and economical method and equipment can be selected for any given condition. This includes accounting methods. Perhaps the cost per inch-mile is, as reported, fifteen times as much in one section as in another; but it is more probable that at least half the difference is due to different methods of calculating the unit costs.

R.

COMMITTEE ON SCIENCE AND THE ARTS.

ABSTRACTS OF REPORTS.

WORK OF DR. JAMES C. IRVINE.

HALL OF THE INSTITUTE,
PHILADELPHIA, FEBRUARY 6, 1929.

No. 2885.

The Franklin Institute of the State of Pennsylvania, acting through its Committee on Science and the Arts, investigating the Work of Doctor James C. Irvine in the Field of Carbohydrate Chemistry, reports as follows:

Sir James Colquhoun Irvine was born in Glasgow in 1877. He was educated at the Royal Technical College, Glasgow and at the Universities of St. Andrews and Leipzig, receiving the degree of Ph.D. from Leipzig, the degree of D.Sc. from St. Andrews and the degree of LL.D. from Glasgow. He has received, also, the honorary degree of Sc.D. from the Universities of Pennsylvania and Yale. He was elected a Fellow of the Royal Society in 1918 and made a C.B.E. in 1921. He was Professor of Chemistry and Dean of the Faculty of Science in the University of St. Andrews until 1921, when he was appointed Principal of this Institution. More than 70 papers on the chemistry of sugars have been published by Sir James and his co-workers, in the Transactions of the Chemical Society.

The elucidation of the structural chemistry of the carbohydrates, which involved the very difficult task of disentangling from each other a series of closely-similar substances, long presented many stumbling blocks which even the finest experimental skill could hardly surmount. The discovery of the phonylhydrazones and osazones by Emil Fischer enabled this celebrated chemist to carry to successful completion, in a relatively short period, a vast research which ended with the determination of the structure and special configurations of

all the known pentoses and hexoses. Although Fischer's researches cleared up the field of the monosaccharides, our knowledge of the polysaccharides remained in almost the same state as it had been before he commenced his brilliant investigations on the sugars.

About the beginning of the century, following an interval of inactivity in the field of the sugars, a third period in the history of carbohydrate chemistry was inaugurated. The new attack was opened in the chemical laboratories of the University of St. Andrews by Purdie and Irvine, and later was conducted for a period of over twenty years by Irvine and his co-workers. According to Holleman, the results of the exceedingly difficult and brilliant researches of Irvine and his coadjutors are mainly responsible for the elucidation of the structure of reducing dioses.

"Like Fischer, the new investigators had armed themselves with a fresh weapon. As phonylhydrazone formation had been the key to the monosaccharides, so methylation was to throw light upon the constitutions of the much more complex carbohydrates."

The methylation of sundry members of the sugar group was rapidly taken in hand. From an examination of the simpler methylated derivatives so obtained, it was possible in a large number of cases to determine the structure of the parent compound. "Galactose, sucrose, and maltose were subjected to methylation; and in 1906 an extension of the method into a further region showed that the new process could be applied to the determination of the structure of the typical natural glucoside, salicin." In 1910, an entirely fresh field was entered upon in Irvine's laboratory, where by means of a new method of methylation, methyl radicals were introduced into cellulose and starch, and Irvine succeeded in attaining a deeper insight into the structure of the molecules of these very complex substances.

"A modification of the new methylation method enabled it to be applied to the preparation of glucosides and methylated glucosides; and the simplification of work in such cases facilitated the constitutional study of sucrose, lactose, maltose, and cellobiose.

"The preparation of these numerous methylated carbo-

hydrates, and the identification of the fission-products of the simpler polysaccharides after hydrolysis, represent in themselves a gigantic piece of work; but to see the matter in true perspective it must be borne in mind that all this labour was undertaken merely as a first step towards the solution of the most intricate problems in the carbohydrate field. Stage by stage, the investigation was consolidating the ground for the final attack upon the constitutions of the most complex naturally-occurring carbohydrates. One by one, the structures of the simple materials were determined; the modes of linking one monosaccharide nucleus to another were established; and it was not until all had been made ready that a real attempt was made to discover the molecular groupings of inulin, cellulose, starch and glycogen. The research has now entered this ultimate stage; and although at present—as Irvine himself has frequently laid down—it is too soon to speak of finality, nevertheless our knowledge of the polysaccharides has grown almost out of recognition within the last few years."

Irvine's work on the methylation of carbohydrates resulted in the gradual accumulation of a mass of evidence which led to the discovery of a new class of sugars—the gamma sugars, in which the oxygen ring is displaced from the normal, stable position.

In consideration of his brilliant researches in the field of carbohydrate chemistry, THE FRANKLIN INSTITUTE awards its ELLIOTT CRESSON MEDAL to SIR JAMES C. IRVINE, Principal of the University of St. Andrews, St. Andrews, Scotland.

WORK OF WILLIAM H. GARTLEY.

HALL OF THE INSTITUTE,
PHILADELPHIA, DECEMBER 5, 1928.

No. 2897.

The Franklin Institute of the State of Pennsylvania, acting through its Committee on Science and the Arts, investigating the Work of Mr. William H. Gartley, of Philadelphia, Pennsylvania, in the Gas Industry, reports as follows:

Mr. William H. Gartley is a native of Philadelphia, Pennsylvania, where he was born on July 17, 1859. He has

spent nearly forty-five years of his life in the gas industry, winning distinction for his engineering accomplishments, and for executive ability as well.

He was graduated from the Polytechnic College of Pennsylvania with the degree of B.M.E.; was a post graduate student at Cornell University; and was graduated from the United States Naval Academy in the Class of 1881, after which he served for two years of sea duty, as was then required before final graduation.

Upon completion of this sea duty, most of the members of that Class were mustered out of the Service, owing to a legislative reduction in the number of officers.

Mr. Gartley was among the large number of the Class who thus returned to civil life.

Soon thereafter he entered the gas business, his first years of service being under T. S. C. Lowe, the inventor of the modern water gas process; in association with Mr. Lowe, Mr. Gartley was engaged in the design, development, construction and operation of gas plants.

He has held successively the following positions in Philadelphia from the dates given: Engineer, Philadelphia Gas Improvement Company, June 15, 1889; Engineer of Works, Philadelphia Gas Works, December 1, 1897; Chief Engineer of Philadelphia Gas Works, March 31, 1926; Vice-President in Charge of Engineering, the Philadelphia Gas Works Company, January 1, 1928.

His work during these many years in the planning, development and operation of the gas works of one of the largest cities of the country has kept him in close contact with many phases and many problems of the manufacture, distribution and use of gas for lighting and heating.

Individually, and in association with others, he has invented a number of devices used in the manufacture and purification of gas, for which the following United States patents have been granted:

Number	Date	Patentee	Title
767,333	August 9, 1904	W. H. Gartley and E. H. Earnshaw	Recuperative Gas Retort Setting
868,603	November 15, 1907	W. H. Gartley	Process of Preparing Illuminating Gas for Distribution
1,232,462	July 3, 1917	W. H. Gartley and S. P. M. Tasker	Means for Receiving and Discharging Coke from Gas Retorts
1,225,237	May 8, 1917	W. H. Gartley	Improvement in Manufacture of Toluol
1,497,010	June 10, 1924	W. H. Gartley and O. B. Evans	Automatic Control of Water Gas Set
1,485,845	March 4, 1924	W. H. Gartley and O. B. Evans	Automatic Control of Water Gas Set

Mr. Gartley and his associates carried on a very considerable amount of research work, the results of which were embodied in improvements in the plants under his charge, and were published in papers presented by him at meetings of societies interested in the manufacture and distribution of gas.

The problem of maintaining the candle power of gas delivered at differing distances along a conduit was an important one for the industry, and one which confronted Mr. Gartley, as the contract between the City of Philadelphia and the Gas Company required the delivery of gas of not less than 22 candle power, measured at testing stations located a mile from each manufacturing plant. This problem was solved by Mr. Gartley with remarkable success. The Institute is informed that for a long term of years, through a period of reconstruction and under very careful city inspection, the standard quality was regularly delivered, and the daily average candle power held within very close limits. The fact of the excellence of the service is generally well known in this community; it is very evident that the accomplishment was a notable one, which has redounded greatly to Mr. Gartley's credit.

The method devised by Mr. Gartley to achieve this result was described in a paper presented by him before a meeting of

the American Gas Institute held in Chicago in 1906 entitled "Delivery of Uniform Candle Power to the Consumer." The reading of this paper was followed by a full discussion; and Mr. Gartley was later awarded the Beal Medal for it, as being "the best paper at the American Gas Institute Meeting of 1906." This was a distinguished honor, as this medal was the most highly prized medal presented by the American Gas Institute.

Mr. Gartley's work has covered a period during which there has been a notable development not only in the manufacture and distribution of gas but in the methods and apparatus used in its measurement and uses. This was particularly true in the field of gas lighting, since the business had advanced so far that the approximate methods previously used were not accurate enough to secure the desired quality and economy.

To obtain information regarding approved methods of determining candle power and the conditions that affect it, a Committee of the American Gas Institute was appointed and Mr. Gartley made Chairman of it. At a meeting of the Institute held in Washington in October, 1907, he presented the results of the findings of that Committee as the "Report of Committee on Methods of Taking Candle Power of Gas."

This report went extensively into the conditions affecting candle power—such as the room in which the measurements are made, its ventilation, the effect of humidity and purity of the air, and other factors. The construction of the photometer room, the type of photometer used and the method of its use were fully described. An account was also given of the most desirable of the working standards then in use, together with a discussion of the requirements to be met by a light unit.

Mr. Gartley's work in connection with the use of gas as an illuminant brought his name prominently before the Illuminating Engineering Society, and he was elected its President for 1909.

An article by Mr. Gartley, entitled "The Gas Business in the Lighting Field," appeared as an editorial in the September, 1914, issue of the *Lighting Journal*, in which issue appears also the following reference to him under the head of Personal Notes: "William H. Gartley, who writes the leading editorial

for this issue, has been allied for a number of years to many progressive movements. Among them the development of modern lighting has been by no means the least; he has been closely allied to the gas industry, more particularly from an engineering standpoint, practically from the beginning of his business career, and is known both in this country and abroad as an authority on the production and other engineering features of gas undertakings."

In 1914 Mr. Gartley was President of the American Gas Institute.

He has given a great deal of attention to the development of by-products, and has contributed much to the advancement of this important phase of gas manufacture.

During the War, he was a member of the Committee on Coal Tar By-Products for the Chemical Committee of the Council of National Defense.

At that time, when it was of the greatest importance that the country should be able to secure all available toluol, Mr. Gartley's knowledge of the subject was of great service to the War Industries Board; of like service was the production of toluol by the gas works in Philadelphia under his engineering operation.

Some years ago the Educational Committee of the Philadelphia Chamber of Commerce began the publication of a series of bulletins having for their purpose "To Make Philadelphia's Life, Industry, History and Government Known, Understood and Appreciated by All Its Citizens."

Number 10 of this series was written by Mr. Gartley and published in 1917, its title being "The Manufacture, Distribution and Use of Gas in Philadelphia." This bulletin treated such subjects as Coal Gas and Water Gas Generating Apparatus; One and Two Section Gas Holders, Gas Governors and Meters; Different Types of Burners and Mantles; Gas Engines; Photometers, etc. Although prepared only for popular use, and of elementary character, this bulletin presents in its sixty-one pages such a large amount of useful information, set out in such a clear and understandable way, as to merit mention. It illustrates well the service an engineer can render to his art by lending his ability to promote intelligent popular understanding of it.

In March, 1924, Mr. Gartley presented a paper on "The Use of Superheated Steam and Superheated Blast in Water Gas Sets" before the joint convention of the Illinois Gas Association, the Illinois State Electric Association and the Illinois Electric Railways Association.

It may justly be said of him that he has contributed notably to the theory and the practice of his art, and has won well merited distinction in both.

In consideration of his engineering contributions to the advancement of the gas industry, to the development and practical operation of large city gas works, of his ingenuity, sound judgment, and service to the public in his field of work, THE FRANKLIN INSTITUTE awards its WALTON CLARK MEDAL to MR. WILLIAM H. GARTLEY, of Philadelphia, Pennsylvania.

WORK OF DR. CHEVALIER JACKSON.

HALL OF THE INSTITUTE,
PHILADELPHIA, APRIL 3, 1929.

No. 2905.

The Franklin Institute of the State of Pennsylvania, acting through its Committee on Science and the Arts, investigating the Work of Doctor Chevalier Jackson, of Philadelphia, Pennsylvania, in Peroral Endoscopy, reports as follows:

Chevalier Jackson was born at Pittsburgh, November 4, 1865, and was graduated from the Jefferson Medical College with the degree of Doctor of Medicine in 1886. He was Professor of Laryngology in the University of Pittsburgh from 1908 to 1916, and at the Jefferson Medical College from 1916 to 1923. He has been Professor of Bronchoscopy and Esophagoscopy in the University of Pennsylvania since 1920 and in the Jefferson Medical College since 1923, and has also been a lecturer in both the Woman's Medical College of Pennsylvania and Temple University. He gave a summer course in his specialty in the Faculty of Medicine of the University of Paris during 1925 and 1927, and will again give this course in 1929.

His researches on peroral endoscopy have been devoted largely to the problem of foreign bodies in the food and

respiratory passages. These researches have involved study of the mechanical principles in the removal of foreign bodies and in the construction of suitable instruments for such removal, and the development of a technique for their use. The instruments include the bronchoscope, the esophagoscope, a special type of laryngoscope, numerous forceps, and a suction apparatus. A unique device on both the bronchoscope and the esophagoscope is the insertion of the source of illumination at the distal end of the instrument in order to produce, as nearly as possible, direct illumination of the field of operation. Approximately 2300 cases have been treated in Doctor Jackson's clinics.

The results of Doctor Jackson's researches have been made known and available through his books, his papers in journals and his instruction of both undergraduate and graduate medical students.

V. E. Negus, F.R.C.S., England, describes his experience in Doctor Jackson's "class," or course, in the Graduate School of Medicine of the University of Pennsylvania, in a British publication—*The Journal of Laryngology and Otology*, 1924, XXXIX, 145–149. He states that he does so "most gladly, as it affords an opportunity for recording my gratitude and my appreciation of a class to which there is nothing comparable in this country, nor so far as I know, in Europe." He also writes: "It would well repay a visit to Philadelphia, if only to make the acquaintance and friendship of the members of the clinic, for everyone who comes in contact with Doctor Jackson is deeply impressed with the extreme charm of his personality, and his intense earnestness in the treatment of patients; not only does he use, to the full, his far from strong constitution in the interest of others, most of whom are of the poor classes, but he generously strives to convey the methods he believes in to his pupils, so that they too may do good work."

Of Doctor Jackson's publications, mention may be made of his "Paroral Endoscopy, Laryngeal Surgery, Bronchoscopy, and Esophagoscopy" which also appeared in French in 1923, and his "Bronchoscopy and Esophagoscopy." He has prepared many of the illustrations for these treatises.

In poisoning by ingestion of caustic poisons, especially household lye, if the patient does not die, severe and perma-

nent injury may be done to the esophagus, including atrosia and stenosis. This fact caused Doctor Jackson to take a prominent part, during a period of seventeen years, in the movement which culminated in the passage by Congress of the Federal Caustic Poison Act of March 4, 1927, "to safeguard the distribution and sale of certain dangerous caustic or corrosive acids, alkalies, and other substances in interstate and foreign commerce."

Among the honors which have been bestowed on Doctor Jackson are the honorary degree of Doctor of Science by the University of Pennsylvania in 1923, the honorary degree of Doctor of Laws by Ursinus College in 1927, the cross of the Legion d'honneur in 1927, the Research Fund Prize of the American Laryngological, Rhinological and Otological Society in 1923, the De Roaldos Medal of the American Laryngological Association in 1927, and the Bok or Philadelphia award in 1927. He is also a Fellow of the American College of Surgeons.

In consideration of his researches on the mechanical principles involved in the removal of foreign bodies from respiratory and food passages, his designs of many instruments for that purpose and his development of a technique for the use of such instruments, THE FRANKLIN INSTITUTE awards its ELLIOTT CRESSON MEDAL to CHEVALIER JACKSON, M. D., Sc.D., LL.D., F.A.C.S., of Philadelphia, Pennsylvania.

NOTES FROM U. S. BUREAU OF STANDARDS.*

GRADUATION OF PRECISION CIRCLES.

DURING the past several months the bureau has been actively engaged on the problem of graduating precision circles for geodetic instruments using the high precision circular dividing engine recently purchased and installed in the constant temperature room (see Technical News Bulletin No. 128, page, 3, December, 1927). It has been necessary, however, to design and construct considerable auxiliary equipment to use with the engine, to make certain changes in the engine itself in order to ensure satisfactory operation for the work which the bureau is required to do, and also to develop proficiency in circle graduation. The graduating of a circle for a geodetic theodolite, in which the readings are made by estimation to tenths of a second by the use of micrometer microscopes, is a very different task from graduating a circle for a surveyor's transit, and the bureau has had many difficulties to overcome.

During the past month two circles were graduated and submitted to the Coast Survey for tests when mounted in the theodolites for which they were made. These tests are not completed but it is uderstood that the preliminary results on one circle show it to be satisfactory for theodolite use.

A further improvement of the dividing mechanism is now being carried out which it is believed will considerably increase the accuracy of graduation. This dividing engine is to be used for graduating precision circles for the Bureau of Standards and the United States Coast and Geodetic Survey; other high precision and special circle graduating will be undertaken, provided commercial firms cannot undertake the work.

* Communicated by the Director.

INTERNATIONAL TECHNICAL CONSULTING COMMITTEE ON RADIO COMMUNICATION.

IN the International Radiotelegraph Convention, adopted at the international conference held in Washington in 1927, provision was made for an International Technical Consulting Committee on Radio Communication. The general regulations adopted at the same time specified that this advisory committee should be formed, for each meeting, of experts representing either governments or private radio operating companies. Meetings were to be held normally at two-year intervals, and the first one was to be convened by the government of the Netherlands.

In accordance with these agreements a meeting has been arranged to take place at the Hague in September, 1929. American proposals for consideration at this meeting have been prepared with great care by a joint committee of government and commercial radio engineers, acting under the auspices of the Interdepartment Radio Advisory Committee. Subcommittees were organized to deal, respectively, with (1) frequency maintenance, (2) systematization of frequency allocation, (3) transmitter interference, (4) research organization, (5) definitions and ratings, and (6) amateur licensing. Members of the bureau's staff have served as chairmen of three of these subcommittees.

Commercial companies in this country are sending about ten representatives to the meeting, and the United States Government will have three official representatives supported by four technical advisers. The three delegates are Maj. Gen. C. M. Saltzman, Member of the Federal Radio Commission, Maj. Gen. George S. Gibbs, Chief Signal Officer of the Army, and Captain S. C. Hooper, Head of the Communication Division of the Navy. The technical advisers include Dr. J. H. Dellinger and Dr. C. B. Jolliffe of the Bureau of Standards.

The first essential for proper allocation and effective use of the radio frequency bands available for communication is uniform and accurate measurement of the frequencies. The best method for comparing frequency measurements of various laboratories is the exchange of quartz piezooscillators. Consequently, in connection with this international meeting

the bureau is sending abroad a portable oscillator with thermostatic temperature control, on which measurements will be made at the national laboratories in France, Germany, Great Britain, and Italy. Comparisons have already been made with the Bell Telephone Laboratories and the Naval Research Laboratory, so that the series of measurements abroad will serve to give a direct comparison between nearly all the laboratories in the world which are doing fundamental work on frequency measurements.

CELLULOSE FROM SUGAR CANE.

At the request of the manufacturer, a sample of alpha-cellulose made from sugar cane was tested for its suitability for use in the rayon industry. Alpha-, beta- and gamma-cellulose, copper number, KOH solubility, ash and iron determinations were made. From the results of these tests the pulp appears to be quite satisfactory for rayon use, as far as the properties tested are concerned. The alpha-cellulose content was high and the copper number quite low, indicating a high degree of purification. The beta- cellulose content and the portion soluble in caustic potash further bear this out. The beta-cellulose made up the difference between the alpha-cellulose content and the total fiber and the portion soluble in KOH was less than 3 per cent. The ash content was very low. Some iron was present but it was a very silght trace.

HOT AQUEOUS SOLUTIONS AS COOLING MEDIA.

Present-day practice in hardening metals is based largely upon the use of oils, water, and the aqueous solutions producing the more rapid cooling, such as sodium chloride brines, sodium hydroxide solutions, and water sprays at ordinary temperatures. There is a large gap between the cooling rates obtained in the customary quenching oils and in water, and this is now usually taken care of by tempering subsequent to hardening or by interrupted quenching. Such procedure is entirely satisfactory for many practical purposes, but simplification and economy, and possibly also technical advantages, would result if coolants were available to provide a more

closely graded set of cooling characteristics. For this reason the bureau has investigated cooling media for quenching steels, and will publish its findings in the September number of the *Bureau of Standards Journal of Research.*

The practical solution of this problem is not solely one of obtaining certain prescribed cooling rates, but this is one of the important requirements. Study of the surface and center cooling curves, hardnesses, and structure of small high carbon steel cylinders quenched in water, sodium hydroxide, sodium chloride solutions, and oils at different temperatures suggested the possibility of using some of the hot aqueous solutions to bridge the gap between the cooling rates obtained with water and oils at atmospheric temperatures.

Experiments with carbon and alloy steel tensile test specimens and gages appear to justify the view that hot aqueous solutions can provide a useful group of coolants with graded cooling characteristics for the hardening of small steel pieces. Final selection must depend upon additional experimental work, but the most promising of the group already studied are given below in order of decrease in the speeds, or increase in the times, of cooling: 5 per cent. caustic soda at 20° C.; 5 per cent. salt at 20° C.; water at 20° C.; 5 per cent. caustic soda at 60° C.; 5 per cent. salt at 60° C.; water at 60° C.; 5 per cent. caustic soda at 80° C.; 5 per cent. caustic soda at 85 or 90° C.

The difficulty of reproducing results in quenching will probably increase as the temperature of the aqueous solution approaches the boiling point of water for reasons discussed in the report, but under suitably controlled conditions it should be practicable to make use of these solutions in practical heat treatment. Likewise, there is a possibility of gaining advantages by decreasing the temperature and changing the concentration and rate of circulation of the liquid in individual cases. In any case, evidence has been given of useful properties in a group of liquids which are inexpensive and generally available for the heat treatment of steels.

MEANS FOR INCREASING RELIABILITY OF FUSIBLE TIN BOILER PLUGS.

FUSIBLE boiler plugs for safeguarding steam boilers against the dangers of low water have been in use for many years, and

since 1852 they have been required in all steam vessels of the American merchant marine, except those equipped with pipe, flash, or coil boilers. They are also used in many factory and locomotive boilers.

In its usual form the fusible plug consists of an externally threaded bronze casing filled from end to end with pure tin, which has a melting point of about 231° C. The plug is screwed into the boiler in such a position that it is about one inch or more above the dangerous low water level, one end of the plug being on the water and the other on the fire side. If the water in the boiler falls below the level of the plug the tin melts and is blown out, thus releasing the steam pressure and serving to prevent burning and possible explosion of the boiler.

On May 11, 1914, a boiler of the steamship "Jefferson" exploded, causing the loss of life of several persons. It was shown that this explosion had resulted from low water and consequent overheating of the boiler plates. This should have been indicated by the melting of the filling of the fusible plug in that region, but the plug was found to be unmelted and apparently sound. The plug was forwarded to the Bureau of Standards for determination of the cause of failure. A thorough investigation showed that the filling contained only traces of the original tin, embedded in a matrix of tin oxide, which upon test showed a melting point of 1600° C. This oxide was distributed in such a form and quantity that it held the full steam pressure and would not have melted before the bronze of the plug casing or even the steel of the boiler plates. Actually such a plug constituted a serious hazard instead of a safeguard.

As a result of this investigation a thorough study was undertaken to determine the causes of the formation of this tin oxide. It was found that as little as 0.3 per cent. of zinc or lead in the tin caused a dangerous deterioration, which was eliminated by insisting upon the use of a tin of high purity, containing not more than 0.3 per cent. total impurities. Since this first work was undertaken 15 years ago the bureau has tested boiler plugs regularly for the Steamboat Inspection Service, and more recently another type of deterioration has been noted, i.e., the formation during service of a hard refractory substance replacing the tin filling in the fire end of the plug.

Special apparatus was devised in which it was possible to test plugs under simulated service conditions of steam pressure and temperature. Through the coöperation of the Steamboat Inspection Service 184 plugs were returned in the condition as removed from boilers of various types including low and high pressure boilers, both coal and oil fired. It was found that about 10 per cent. of all plugs would not function when subjected to steam of a temperature slightly above the melting point of tin. The failure of the plugs to function was due in every case to the presence of a refractory material in the fire end consisting principally of oxides of copper and tin and in some instances of CaO and MgO. It was shown that the formation of tin and copper oxides was the result of a partial melting of the tin filling and subsequent oxidation. The calcium and magnesium oxides were shown to have come from the boiler water through a leak in the plug because of incomplete bonding of the filling to the casing. As a result of the investigation changes in the existing specifications for fusible plugs were recommended to the Steamboat Inspection Service which it is believed will prevent the crust formation and thus further insure the proper functioning of this valuable safety device.

SECOND PROGRESS REPORT ON SOIL-CORROSION STUDIES.

THE Bureau's Technologic Paper No. 368 set forth the general plan of the soil-corrosion tests on pipe materials which were begun in 1922, and gave the results of observations on specimens taken up for examination in 1924 and 1926. A second progress report including results of examination of the 1928 specimens has now been published as Research Paper No. 95 in the August number of the *Bureau of Standards Journal of Research*. This paper will soon be obtainable by purchase separately from the Superintendent of Documents, Government Printing Office.

The specimens treated in this paper include only ferrous pipe materials and cable sheaths. Soil characteristics, rather than differences in the composition of the ferrous pipe materials, appear to determine the type and extent of the corrosion observed. Tables in the paper show the relative corrosiveness of soils as indicated by rate of loss of weight and rate of in-

crease in depth of pits. Although it happened that the same soil was worse from both of these points of view, the soil that ranked next to the worst from the standpoint of pitting ranked twenty-eighth as to loss of weight. As the specimens in the ground grew older the corrosion became more general, and in most soils there was a decrease in the rate of penetration. Field examination of cast-iron gas mains in several cities yeilded data of a similar nature.

Considerable work has been done recently on methods of predetermining the corrosiveness of soils. The problem has not been solved.

Preliminary studies indicated that, in addition to the localized galvanic action caused by mill scale, differences in oxygen concentration, and other conditions, there are on pipe lines galvanic currents that result from the passing of the line through different soils. There appeared to be a relation between the discharge of these galvanic currents and the corrosion observed on the pipe line.

Additional specimens of pipe materials and coatings will probably be removed in 1930. In the meantime the bureau is compelled to reiterate its former conclusion that no valid comparisons of the length of service of various materials can yet be made on the basis of the data obtained in this investigation.

RESISTANCE OF METALS SUITABLE FOR DIES TO THE ABRASIVE ACTION OF PLASTIC CLAY.

THE abrasive action of plastic clay in flowing through dies wears the liners rapidly and makes necessary frequent renewals. Although it is well known that different metals show different resistances to the abrasion of plastic clay, no data appear to be available showing the relative "wear values" of diffrent metals, such as those used for lining dies. Such an investigation has therefore been undertaken by the bureau.

The work includes tests on different kinds of cast iron, steel, and bronze. Up to the present time 10 tests have been made on cast iron and 44 on carbon-chrome steel.

During each test a definite volume of clay is extruded through the die specimen in a definite time and the abrasive loss of the die is expressed in terms of volume. This is de-

termined by dividing its loss in weight by the specific gravity of the metal.

A very small decrease in water content of the clay produces a marked increase in the pressure necessary to extrude the clay at a definite rate, and the abrasive loss of the die increases with the extrusion pressure. The data obtained from 54 tests indicate that the relation between extrusion pressure and abrasion loss of the metal is a "straight line" function according to the equation $PS/W = K$ in which "P" is the extrusion pressure, "W" the loss of the metal in weight, "S" the specific gravity of the metal, and "K" is a constant characteristic of the wearing quality of the metal.

Metals of highest resistance to abrasion will give the highest K values. The value of K for the cast iron die as compared to that for the carbon-chrome steel die is as 1 to 10.116 which indicates that a clay column can be extruded from a carbon-chrome steel die ten times longer than that from the cast iron die before the two dies show equal abrasive losses.

COMPRESSIVE STRENGTH OF CLAY BRICK WALLS.

THE October number of the *Bureau of Standards Journal of Research* will give a description of an investigation of the compressive strength of brick walls.

Results will be reported of compressive tests of 168 walls of common brick, each 6 feet long and about 9 feet high, and of 129 wallettes, about 18 inches long and 34 inches high. Four kinds of brick, three mortar mixtures, two grades of workmanship, different curing conditions, and ten different types of masonry, three solid and seven hollow, were the variables.

A very complete study was made of the strength properties of the brick. Compressive tests edgewise and flatwise, wet and dry; transverse tests edgewise and flatwise; tensile tests of whole brick, and absorption tests were made, each average being obtained from tests of 50 bricks of each kind. Shearing tests on a smaller number of samples were also made.

The results of these tests lead to the following conclusions:

1. The average strengths of solid walls built of end-cut Chicago brick (average compressive strength of half bricks flatwise, 3,280 lbs./in.^{2}) were as follows:

Lime mortar walls	287 lbs./in.²
Cement-lime mortar walls	587 lbs./in.²
Cement mortar walls	661 lbs./in.²

A contract for building tests walls was let, on a lump sum basis, to a brick mason who specialized in small contracts. The work was done without supervision and was characterized by absence of mortar in the longitudinal vertical joints and deep furrowing of the horizonal beds.

2. With carefully supervised workmanship, the average strengths of solid walls which were built by another mason hired by the day without regard to output and which had completely filled vertical joints and smooth spread horizontal mortar beds were as follows:

Chicago brick: Compressive strength of half brick flatwise, 3,280 lbs./in.²; average compressive strength of solid walls; cement-lime mortar, not determined; cement mortar, 895 lbs./in.².

Detroit brick: Compressive strength of half brick flatwise, 3,540 lbs./in.²; average compressive strength of solid walls; cement-lime mortar, 945 lbs./in.²; cement mortar, 1,145 lbs./in.².

Mississippi brick: Compressive strength of half brick flatwise, 3,410 lbs./in.²; average compressive strength of solid walls; cement-lime mortar, 1,300 lbs./in.²; cement mortar, 1,550 lbs./in.².

New England brick: Compressive strength of half brick flatwise, 8,600 lbs./in.²; average compressive strength of solid walls; cement lime mortar, 1,875 lbs./in.²; cement mortar, 2,855 lbs./in.².

3. The strengths of the solid walls were more closely related to the shearing strength of the bricks than to any other strength property measured. The compressive strength of the half bricks flatwise appeared to be the next best measure and was better than the compressive strength on edge, the modulus of rupture, or the tensile strength of the bricks.

4. On the average, the compressive strength of the wallettes was by far a more consistent measure of the strength of the walls than any of the brick strength values. In predicting wall strengths from brick strengths, effects of mortar and workmanship must be taken into account, while from wall-

ette strengths, only a single value need be determined. These tests show that the average strength of the walls was from about 60 to 90 per cent. of the average wallette strength.

5. The strength of the solid walls which were built by contract varied about as the cube root of the compressive strength of the mortar cylinders (2 inches in diameter and 4 inches long) which were made from the mortar of the walls and cured under the same conditions. For the solid walls built under careful supervision, the increase in strength for cement mortar walls over those laid in cement-lime mortar was about 20 per cent. for walls of Detroit and Mississippi brick and about 50 per cent. for walls of New England brick while the average ratio of the cube roots of the mortar cylinder strengths (cement and cement-lime mortars) was 1.38.

6. With brick, the cross sections of which closely approximated rectangles, the strengths of the hollow walls varied about as the net areas in compression. When the bricks were warped, the strength of the hollow walls was found to be less than that expected from the net area.

7. Construction data show that there is a saving in materials and in time for hollow walls of brick as compared with solid walls.

8. The condition of the horizontal mortar beds in the walls affected the wall strength. Walls in which the beds were smooth were stronger by from 24 to 109 per cent. than walls in which the mortar beds were furrowed.

9. Walls laid in cement mortar and kept damp for seven days after construction were not stronger at the age of 60 days than similar walls cured in the laboratory under ordinary conditions.

10. The results of the wallette tests in which the same variables occured as in the larger walls, lead in general, to the conclusions deduced from the wall tests.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

VARIATION OF THE THRESHOLD SPEED OF AN EMULSION ACCORDING TO THE DEVELOPER AND CONDITIONS OF DEVELOPMENT. III.[1]

E. R. Bullock.

BUT little if any influence on the maximum threshold speed has been observed on varying (1) the interval between exposing and developing, (2) that between preparing and using the developer, (3) the temperature of the developer, (4) the temperature, and (5) the humidity of the sensitive film at the time of exposure. Use of the developer at a lowered temperature showed, however, the effect of a diminution in fog. Some of the ways in which a sensitive film is permanently affected by treatment with silver nitrate solution have been examined in detail. In general, latent fog is produced, and with this an increase in the maximum threshold speed, consistently observed under suitable experimental conditions, appears to be associated.

THE FUNCTION OF GELATIN IN PHOTOGRAPHIC EMULSIONS.[2]

S. E. Sheppard.

THE protective colloid action of gelatin in relation to precipitation and reduction of silver halides is discussed in terms of the chemical constitution of gelatin. It is suggested that imino-(−NH) groups of the protein play a direct part by coördination of silver. The existence of keto-piperazines in gelatin is also considered, and it is suggested that reversible pH control of sensitivity may be connected with this.

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* Communicated by the Director.

[1] Communication No. 268 from the Kodak Research Laboratories and published in *Sci. Ind. Phot.* **9**: *24. 1929.*

[2] Communication No. 384 from the Kodak Research Laboratories and published in *Phot. J.* **69**: *330. 1929.*

SOME PROPERTIES OF FINE-GRAIN DEVELOPERS FOR MOTION PICTURE FILM.[3]

H. C. Carlton and J. I. Crabtree.

THIS paper describes experiments on (*a*) exhaustion tests, (*b*) methods of using the solution for machine development, (*c*) variation of the developer components to satisfy special requirements, and (*d*) methods of obtaining finer-grained negatives.

(*a*) With the rack and tank system, the present published formula works satisfactorily until about eighty feet of panchromatic film per gallon have been processed. Revival with a solution containing half the original quantities of elon, hydroquinone, and borax permits an additional eighty feet per gallon to be developed when the solution should be discarded.

(*b*) The rate of development may be increased by increasing the borax concentration up to twenty grams per liter. The development rate may be decreased and the graininess decreased slightly by lowering the concentration of developing agents and borax to one-half that present in the regular formula. This latter formula is very suitable for machine development. Hydrated sodium sulfate can be added to one hundred grams per liter to reduce further the rate of development and the graininess.

(*c*) The rate of development can be controlled for special requirements by using eight grams of boric acid and eight grams of borax per liter in the usual formula. By varying these quantities but also keeping the total constant, the development rate can be increased or decreased as desired. High concentration of boric acid gives a solution which becomes exhausted more rapidly.

(*d*) Graininess of images can be improved in three ways: (1) by increasing the sulfite to give increased solvent action (recommended only when the developer can be discarded at frequent intervals); (2) by decreasing the rate of development by using a solution containing less alkali and reducing agents;

[3] Communication No. 388 from the Kodak Research Laboratories and published in *Amer. Cinemat.* 10: *17, 1929*, and read before the Society of Motion Picture Engineers, New York City, May, 1929.

(3) by development of the negative to a relatively low gamma and the positive to a relatively high gamma.

The developer can be used for development of positive film but other than reducing the propensity of the solution to aerial fog, it possesses no advantages for this purpose over other developers.

Scientific Research on Bricklaying.—The Multiple Industrial Fellowship on Portland Cement of Mellon Institute of Industrial Research and the Eastern Face Brick Manufacturers' Association have recently inaugurated a broad scientific study of the problems of bricklaying. So many factors are involved in the construction of a brick wall that it is necessary to limit the investigation to combinations of variables most likely to occur in actual practice. The project has been under discussion for a considerable period of time; experiments were begun by Dr. F. O. Anderegg, Senior Industrial Fellow at Mellon Institute, and his assistants only after a satisfactory program had been worked out.

At the present time over 300 experimental brick walls or panels have been erected in order to find the most suitable combinations of materials and workmanship. The following problems are being investigated: the rate of absorption and total absorption of moisture by brick; the surface characters of brick; the merits of different cementing materials, ranging from pure lime to pure cement, and of various sands and mortar pigments; the effect of varying the type of backing, both as to material and size of unit; the results of variation in workmanship, including pointing, tapping, and the filling of head-joints; the effect of variation in design, involving a study of coping and parapet construction, of capillary contact, of condensation, and of elasticity; and the behavior of mortar with reference to the other variables in all types of climatic conditions. All results of these studies will be published for the benefit of every one interested in building construction.

R.

THE FRANKLIN INSTITUTE.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, September 18, 1929.)

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MR. M. M. BORDEN, Chief Engineer, Simplex Valve and Meter Company, 68th and Upland Streets, Philadelphia, Pa.

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DR. F. W. HIGHTOWER, Chemical Engineer, The Barrett Company, Margaret and Bermuda Streets, Philadelphia, Pa.

MR. PAUL E. TODD, Mechanical Engineer, In care of Brown Instrument Company, Wayne Junction, Philadelphia, Pa.

MR. KENNETH URQUHART, Chemical Engineer, Foster Wheeler Company, 165 Broadway, New York City. For mailing: Hotel Paulsboro, Paulsboro, New Jersey.

NON-RESIDENT.

MR. CHESTER L. DAVIS, Electrical and Radio Engineering, 212 Ouray Building, Washington, D. C. For mailing: Apt. 4, 909 Twentieth Street, N. W., Washington, D. C.

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MR. RUSSELL G. THOMPSON, North East Appliances, Inc., Rochester, New York.
DR. ROBERT H. WILHELM, 345 Windemere Avenue, Lansdowne, Pa.
MR. G. H. WOODROFFE, Manager, Boiler Tube Department, Reading Iron Company, 230 Park Avenue, New York City.

LIBRARY NOTES.

RECENT ADDITIONS.

American Gas Association. Tenth Annual Convention, 1928. Proceedings.
American Institute of Electrical Engineers. Transactions July 1929. Volume 48, Part 3.
Beilsteins Handbuch der organischen Chemie. Vierte Auflage. Band XII. 1929.
Central High School of Philadelphia. Hand Book 1928–1929.
International Congress of Photography. Proceedings of the Seventh Congress, 1928.
RÜDISÜLE, A. Nachweis, Bestimmung und Trennung der chemischen Elemente. Band VII, erste Abteilung: Schwefel. 1929.
TYRRELL, G. W. The Principles of Petrology. No date.
WIEN, W., AND F. HARMS, editors. Handbuch der Experimentalphysik. Band 22. 1929.
World Power Conference. Power Resources of the World. 1929.

BOOK REVIEWS.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 311. Aerodynamic Theory and Test of Strut Forms by R. H. Smith. 24 pages, illustrations, quarto. Washington, Government Printing Office, 1929. Price, ten cents.

The whole study under this title is in two parts, only the first of which is reported here. In this part the symmetrical inviscid flow about an empirical strut of high service merit is found by both the Rankine and the Joukowsky methods. The results can be made to agree as closely as wished. Theoretical stream surfaces as well as surfaces of constant speed and pressure in the fluid about the strut are found. The surface pressure computed from the two theories agrees well with the measured pressure on the fore part of the model but not so well on the after part. From the theoretical flow speed the surface friction is computed by an empirical formula. The drag integrated from the friction and measured pressure closely equals the whole measured drag. As the pressure drag and the whole drag are accurately determined, the friction formula also appears trustworthy for such fair shapes.

R.

NATIONAL RESEARCH COUNCIL, BULLETIN No. 71. Bibliography of Bibliographies on Chemistry and Chemical Technology. First supplement 1924–1928. 161 pages, 8vo. Washington, The National Research Council, 1929. Price $1.50.

This, the First Supplement to the Bibliography of Bibliographies on Chemistry and Chemical Technology, covers the period 1924–1928, Bulletin No. 50 having covered the period 1900–1924. This Supplement contains approximately 4100 bibliographies classified under 1050 headings. The original Bulletin (No. 50) contained approximately 10,000 bibliographies classified under 2400 headings.

As the title indicates, the work (as in the case of Bulletin No. 50) is a compilation of bibliographies published as separates, or at the end of books or magazine articles, or as footnotes to the same, on the numerous aspects of pure and applied chemistry. Each entry gives name of author or compiler, title, and place of publication. The majority of the entries state the number of references, thus giving an indication of the completeness of the particular bibliography. The entries are classified under the proper subject-headings, alphabetically arranged. The duplication of individual entries has been largely avoided by the liberal use of cross references.

As an example of the value of this compilation, the following information is given regarding the number of bibliographies reported for some of the more important topics: Blood chemistry 25, Cement 21, Coal 31, Colloids 55, Dielectrics 24, Dyes and Dyeing 27, Fertilizers 38, Fibres 26, Foods 33, Iron and Steel 76, Metabolism 77, Milk 43, Mineral Resources, 25 Paper 39, Petroleum 54, Photography 36, Plant chemistry 41, Rubber 55, Vitamins 25, Water 45.

R.

ONDES ET ELECTRONS. Par Pierre Bricout, Docteur es sciences, Repetiteur a l'Ecole Polytechnique. 215 pages, illustrations, 16–20 paper (No. 113, Collection Armand Colin). Paris, Librairie Armand Colin, 1929. Price, bound 10 francs 25; paper 9 francs.

There is undoubtedly a large class of readers of scientific literature who desire a connected account of the subjects of atomic physics and radiation, the diversity of phenomena which they embrace, and the theories of atomic structure and the mechanism of wave-motion employed in their development. There is a comprehensive collection in treatise form now available of the numerous topics which enter into this important field, but the task of perusing such treatises is far beyond the requirements or inclination of readers who seek a rational and, as far as possible, deductive general survey. The present volume is written to supply this need.

In the unusually compact form which is characteristic of the collection Armand Colin, M. Bricout gives an explanation of the experimental and theoretical investigations which constitute the foundations of present-day atomic physics. Beginning with the commonly known properties of electrical charges and the effect of the dielectric, he passes to a consideration of the discharge of electricity through gases, cathode rays, thermionic and photoelectric phenomena, and radio-activity about which electronic theory has proceeded. With that logical introduction the reader is prepared for the multiplicity of topics on the electronic theory which follow. The list is a long one; indeed nothing appears

to have been omitted in the arrangement and skilfully summarized treatment of representative topics. In the mathematical discussion of much of this matter, the vectorial calculus is freely employed. Anticipating some difficulty on the part of the reader with this method of analysis, the author refers to "Calcul Vertoriel" by Raoul Bricard in the same series as covering the essentials of that subject.

The work is a comprehensive syllabus of modern atomic physics in small compass with a generous amount of explanatory matter. L. E. P.

PROFESSOR COKER'S PHOTO-ELASTIC APPARATUS, FOR DETERMINING THE DISTRIBUTION OF STRESS IN STRUCTURAL AND MACHINE MEMBERS. Anonymous. 28 pages, illustrations, 8vo. London, issued by Adam Hilger, Ltd.

The beautiful color effects in strained transparent material when viewed by polarized light have long been known, and striking lithographs in color illustrating these figures are to be found in most of the notable text-books of physics of an earlier generation. The idea of utilizing these figures to indicate the presence of internal stresses was suggested, also, many years ago. Professor Coker's researches, which are relatively recent, have been of a most searching character, and from them has been evolved a system of determining the internal stresses of structural parts. These results have been translated into a system of procedure and an equipment for straining a specimen and viewing the effect by polarized light of which Messrs. Hilger are the makers. The present pamphlet is descriptive of this equipment with an account of the principles of the procedure and other data of value in this method of determining internal stresses. Celluloid $\frac{1}{8}$ to $\frac{1}{4}$ of an inch in thickness is employed for the specimens to be tested, the stresses being independent of the material provided it is isotropic, and depending solely upon the form and manner of loading. L. E. P.

THERMOMETRIC CONVERSION CHART. For the use of mathematicians, chemists physicists, schools, etc. By Percy L. Marks, L.R.I.B.A., Chartered Architect, author of "Principles of Planning Buildings," etc. 6 pages, 26 x 19 cm., with folding plate, cloth. London, Crosby Lockwood & Son, 1927. Price 3/6.

Apart from scales for the measurement of linear dimension there is scarcely any instrument more familiar to all classes of persons or more widely used than the common form of thermometer. To facilitate conversions, the author has prepared a chart of parallel-arranged scales of the commonly used systems including the absolute scale (degrees Kelvin) and the now little known De L'Isle scale in which the boiling point of water is marked "0" and the melting point of ice is marked "150." The chart is well executed and excels a tabular arrangement of values in that tenths of degrees may be read, a subdivision that would make the usual tabular arrangement of awkward size. The chart requires a tee-square or equivalent for accurate readings. Numbered equally divided scales on opposite sides of the chart might be provided for squaring a straight-edge or silk thread, so avoiding the need of a square. An introduction contains brief historical notes relative to the originators of the several scales which are included on the chart. Despite the author's opinion to the contrary, there is a very considerable bibliography on thermometry in European countries.

LUCIEN E. PICOLET.

PUBLICATIONS RECEIVED.

National Research Council, Bulletin No. 71. Bibliography of Bibliographies on Chemistry and Chemical Technology, First Supplement, 1924–1928, compiled by Clarence J. West and D. D. Berolzheimer. 161 pages, 8vo. Washington, National Research Council, 1929. Price, $1.50.

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CURRENT TOPICS.

The Infra-red Spectra. SIR ROBERT ROBERTSON. (*Nature*, June 15, 1929.) An excellent view of the present status of our knowledge of infra-red spectra is presented in this lecture delivered at the Royal Institution on March 1, 1929. In 1800 Herschel showed that a thermometer, placed beyond the red end of the spectrum, indicates a rise of temperature and thus gave the first experimental proof of the existence of the infra-red region. From the middle of the nineteenth century onward much interest has been shown in this field of the spectrum and instrument after instrument has been fitted to the needs of its investigation. Abbey by photography recorded the spectrum for a short distance beyond the visible red. "Langley with the bolometer, Boys with the radiomicrometer, and Coblentz with the thermopile, succeeded in measuring quantitatively radiation in the infra-red: the last two instruments are the principal ones employed to-day in that region which lies nearest to the visible. Still farther out, measurement of the energy in the beam dispersed by means of reflection from the polished surface of crystals gave important results in the hands of Rubens and his colleagues, while within the last year Raman by an entirely different technique has indicated how infra-red radiations can be deduced from spectroscopic measurements in the visible spectrum."

The infra-red spectrum contains bands due to the vibration of atoms within the molecule and to the rotation of the molecule itself. To the vibration are ascribed the chief bands, while the rotation of the molecule causes bands of simple character in the far infra-red and other bands in the near region that appear as fringes to the other type. Important information is derived from the study of the infra-red spectrum, such as the frequency of the vibration of atoms within the molecules and of the rotation of molecules, moments of intertia of molecules about different axes and the lengths of molecules. Yet much more concrete conclusions have been drawn. Coblentz has thus studied the quantity of radiation from stars and planets and has derived their temperatures. Even the radiation differences of the hemispheres of Mars have not eluded him. Further, G. C. Simpson, employing what is known of the infra-red spectrum of water vapor and of carbon dioxide has reached the surprising conclusion "that an increase in solar radiation would

result in increased cloud and precipitation, and even in the apparent paradox of an ice age."

Because the main part of the radiation emitted in combustion is in the infra-red much work must be done here to elucidate what takes place in flame and in explosion.

"Like the X-rays, the infra-red deals with the structure of the molecule, but while X-rays reveal the molecule in its static condition and are especially applicable to solids, infra-red spectra reveal the dynamic characteristics of the molecule in gases, liquids, and to a restricted degree in solids. In the future it will undoubtedly be used to a greater extent in the determination of the nature of chemical linkages and generally for the solution of problems of chemical constitution. The molecule as a dynamical entity has been comparatively neglected." G. F. S.

World's Power Congress, Berlin, 1930. The second World Power Conference will be held in Berlin, June 16 to 23, 1930. The subjects for discussion will include the development of power and power utilization, new methods of the application of power, efficient utilization of generating plants and distribution networks, the storage of power, advantageous interconnection of different power producing plants, large central plants and large power distributing systems, propaganda and tariff systems, administration and legislation, safety measures, standardization, statistics, and education.

Papers submitted to the Conference will be printed and distributed in order that those attending the meetings may take part in the discussions.

In addition to the general sessions there will be a number of visits to electrical and gas plants in Berlin, to the works in central Germany, especially those using brown coal, to the plants in the Rhineland, Westphalia, East Prussia and Silesia and to the German Museum in Munich, the water power and steam plants in Bavaria and Baden.

Subcommittees composed of about three hundred German specialists are engaged in preparing the programmes for the meetings and visits. Headquarters of the Conference are in the house of the Verein Deutscher Ingenieure, Berlin. R.

When the General Board of the National Physical Laboratory made its annual visitation to the laboratory at Teddington, England, many interesting exhibits and experiments were displayed. Apparatus was shown for measuring the heat that becomes latent in wire-drawing. The die was situated within a Dewar flask that served as a calorimeter. An alloy of nickel-chromium-iron exhibited

had an ultimate breaking stress of 30 tons per sq. in. at 800° C., and did not break at this temperature when 5 tons per sq. in. were supported by it for 68 days.

Sabin's measurements of the absorption of sound have been greatly refined. His organ pipe for the production of the sound whose decay was to be studied is replaced by a valve oscillator and loud speaker and, instead of the ear of the observer, a microphone, receiving set and reflecting galvanometer register on photographic paper the decrease of the intensity of the sound, with a tuning fork to measure time intervals.

X-ray intensity is measured by an apparatus where the rays traverse an ionization chamber and a string galvanometer furnishes the strength of the ionization current.

The presence of tangential stresses when a dielectric is subject to a three-phase electric field was demonstrated by mounting a cylinder of paper at the center of a three-field. The field made the cylinder rotate.

"In the William Froude Tank a novel method of determining the wind resistance and center of effort of ship superstructures by measurements in water was demonstrated. The superstructure complete with funnels, masts, derricks, etc., is towed upside down through water at slow speeds." The resistance in air can be calculated from the resistance measured in water. (*Nature*, July 6, 1929.)

G. F. S.

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